Center for Materials Science

Polymer Science and Standards Division

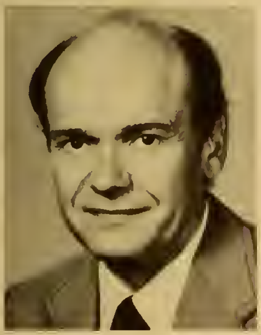
Annual Report 1979

Plastics

U.S. DEPARTMENT
OF COMMERCE
National Bureau
of Standards

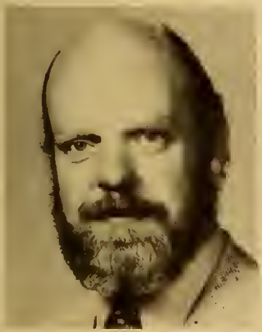
Polymer Science and Standards Division

Ronald K. Eby, Chief. Dr. Eby was born in Reading, Pennsylvania in 1929. He earned the Sc.B. in physics at Lafayette College and the Sc.M. and Ph.D. at Brown University. Before joining NBS in 1963, he conducted polymers research in the Plastics Department of E. I. du Pont de Nemours & Co.



Darrell H. Reneker, Deputy Chief. Dr. Reneker was born in Birmingham, Iowa in 1929. He earned degrees in engineering at Iowa State University and in physics at the University of Chicago. Before joining NBS in 1969, he worked for Bell Laboratories and E. I. du Pont de Nemours & Co.

Anton Peterlin, Assistant Chief. Dr. Peterlin was born in Yugoslavia in 1908. He earned the M.S. in mathematics at the University of Ljubljana and Ph.D. in physics at the University of Berlin. From 1939 to 1960, he was professor of physics in Ljubljana and from 1949 to 1959 was head of the Josef Stefan Institute. Before joining NBS in 1973, he was director of the Camille Dreyfus Laboratory.



Martin G. Broadhurst, Chief, Bulk Properties. Dr. Broadhurst was born in Washington, D.C. in 1932, and earned degrees in physics at Western Maryland College and Pennsylvania State University. After teaching at Penn State, he joined NBS in 1960.

Leslie E. Smith, Chief, Stability and Standards. Dr. Smith was born in New York in 1941. He earned degrees in chemistry from Case Institute of Technology and Catholic University. Except for a three year period of graduate study, he has been with NBS since 1964.

Bruno M. Fanconi, Chief, Structure and Properties. Dr. Fanconi was born in Merced, California in 1939. He earned degrees in physical chemistry from the University of California at Los Angeles and the University of Washington. He joined the staff of NBS in 1971.

James M. Cassel, Chief, Dental and Medical Materials. Dr. Cassel of New Kensington, Pennsylvania was born in 1918 and earned the Ph.D. in chemistry at Georgetown University. He joined NBS in 1946 and today guides a program of research for improved dental and medical restorative materials.

POLYMER SCIENCE AND STANDARDS DIVISION

Annual Report 1979

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POLYMER SCIENCE AND STANDARDS DIVISION

Ronald K. Eby, Chief
Darrell H. Reneker, Deputy Chief
B. M. Weeks, Secretary
H. E. Kistler, Secretary

In the 70 years since Baekeland introduced the first commercial plastic produced entirely by the reaction of small molecules, plastics have left little of our culture and our technology untouched. We have moved rapidly into an age in which an overwhelming number of the needs of mankind are served by plastics.

Important trends in the polymer industry include increased use of polymers in packaging, in automobiles to reduce weight and improve fuel economy, in electronic and information handling applications, and in medical implants. These increasingly sophisticated and demanding applications have created new needs for concepts, measurements, standards, and data that can be used to insure that plastics perform as intended not only in the use environment, but in processing and other phases of the materials cycle as well.

A number of long-range planning activities were carried out. These included visits by the Division managers to the polymer research laboratories of Proctor and Gamble, Army Research and Development Command, General Motors, Boeing Commercial Airplane, and Lawrence Livermore Laboratory.

The costs associated with the limited durability of plastics were estimated by a survey of industrial trade associations and academic sources. It appears that this survey is the first of this sort ever attempted for plastics. The uncertainties in our estimates are therefore large because of the sparse data base. Significant economic costs related to limited durability appear in the following applications of polymers: Building, Transportation, Energy Transmission, Appliances, Dental and Medical Applications. Costs associated with limited durability of plastics in all areas appear to be in the range of 6 to 12 billion dollars per year.

A survey of polymer processing science and technology was also completed. Attention was focused on the processing of polymer blends and on the biaxial orientation of polymers because of the large growth potential of these processes. Many contacts with experts in industry and university laboratories were made to gather information about the future prospects for these areas of polymer processing. The report also contains information about more conventional polymer processing methods, including injection molding, extrusion blow molding, thermoforming, structural foaming, rotomolding and reaction injection molding.

These planning activities help insure that the future efforts of the Division will be responsive to the themes outlined by the Director of NBS in his State of the Bureau address. These are the healthy growth of industrial productivity, prudent utilization of energy sources, a reasonable system for the regulation of the effects of technology and a wise policy of materials utilization.

Major problems now being addressed by Division projects include:

- A cooperative effort with the Bureau of Foods to produce methods of improved reliability for predicting both the rates of migration of small molecules from plastic containers into foodstuffs and the equilibrium concentrations that will be reached.

- Elucidation of the molecular level processes that are responsible for piezoelectric effects in polymers. Applications of devices based on piezoelectric polymers led to solutions of measurement problems ranging from improved control of presses used to print currency to monitoring the intensity of ultrasonic energy used in medical diagnosis and treatment.

- Evaluation of the fatigue resistance of elastomers needed in efforts supported by the National Institutes of Health to develop artificial heart components and improved circulatory assist devices.

- Improved polymer-based dental restorative materials and adhesives to make durable bonds between restorative materials and tooth tissue. This work involves extensive cooperation with the American Dental Association and the National Institute for Dental Research.

- Characterization of the elastomers used as seals in equipment used to collect energy from geothermal sources in Department of Energy sponsored projects. More durable elastomeric seals will allow greater use to be made of this potentially large and cost effective energy source.

- The mechanical durability and permeation behavior of plastics used in containers for the safe transport of hazardous materials needed to insure reasonable regulation of such containers by the Office of Hazardous Materials of the Department of Transportation.

These problems and the others detailed in the following pages lead the scientists in the Division into productive examination of those properties of polymers which are (or should be) of concern to people who design and produce useful objects from plastics. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of plastics.

The activities of the Division are associated into six Tasks, each described separately below. The Task titles are:

DIELECTRIC PLASTICS DESIGN AND PERFORMANCE

POLYMER STANDARDS FOR CONTROL AND EQUITY

CHEMICAL DURABILITY OF POLYMERS IN USE

MIGRATION AND THE DURABILITY OF PLASTICS IN USE

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE

TESTS, STANDARDS AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

DIELECTRIC PLASTICS DESIGN AND PERFORMANCE

M. G. Broadhurst

Task Leader

Trends in dielectric application of polymers include use of higher working voltages in electrical apparatus and transmission lines to conserve materials, save space, and reduce weight. This work provides manufacturers (polymer manufacturers, film fabricators, transducer manufacturers), trade associations (EPRI), and government agencies (DoE, DoD) with data, measurement methods, and concepts which identify limitations in polymer performance traceable to manufacturing practices. For example, steam curing of extruded polyethylene insulated cables results in lifetime limiting voids and inclusions. With a trend toward increased use of underground transmission of electric power, improved insulation performance is required. Data and recommendations from this work go directly to cable manufacturers and funding organizations (i.e., EPRI, DoE) who are able to specify and require manufacturing changes leading to improved products.

Other trends are new, rapidly growing applications of polarized polymers as pyro- and piezoelectric transducers. Transducer manufacturers as well as private and government transducer users (DoD, EPA, HEW) need reliable information connecting polymer structure and polymer performance to the design of improved transducers. This work will help transducer material and device manufacturers design and develop commercial polymer transducers for use in health and safety applications (pulse monitors, therapeutic and diagnostic sound measurements, auto crash sensors, prosthetic fitting devices, nontoxic antifouling coatings, mine disaster warning devices) and in the areas of national security (microphones, hydrophones, intrusion detectors, ultrasonic and infrared imaging devices, fusing devices, etc). Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement methods which are becoming possible with newly developed polymers. For example, this work attempts to show how polymers interact with electronic and ionic charges, and how structure can be modified to optimize piezoelectric, pyroelectric, and semi-conducting properties.

Polymer Insulation for Superconducting AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

This project, sponsored by and carried out in collaboration with Brookhaven National Laboratory (BNL) with DoE funds, is part of a program for evaluating the suitability of various types of polymer films for use (in tape form) as the electrical insulation in high power superconducing AC transmission cables operated at 6 K - 9 K. Such cables, in which the superconductor is Nb_3Sn, are currently under development at BNL. Among the guidelines used for selecting the insulation for such cables is that the dielectric constant (ε) should be 2.5 or less, and that the dielectric loss ($\tan \delta$) should preferably not exceed 20×10^{6} at the cable operating range and 60 Hz.

This subtask is primarily concerned with the measurement of the dielectric properties (ε, $\tan \delta$) of polymer films at cryogenic temperatures. These measurements, for which NBS has a unique instrumental facility, are coupled with studies of aspects of the fine structure of the films in an effort to determine the influence of various structural parameters (e.g., crystallinity, molecular orientation, voids) on the dielectric properties of the films. In addition to determining whether specific types of commercially available films meet the established criteria for dielectric properties, these studies are aimed at providing data relevant to the design and production of films exhibiting optimum dielectric properties for the intended end use. In a less extensive effort, the compressibility of the polymer films is measured. This latter feature is among others, relevant to the determination of the optimum conditions (e.g., tape tension) necessary for winding the films (slit in the form of tapes) around the cable core, so as to yield a cable exhibiting appropriate flexibility for winding onto storage drums 10 ft. in diameter.

For FY 1979 the main concern was to characterize the dielectric loss of laminates consisting of polypropylene tapes bound together with a polyurethane adhesive. The laminates were made in order to form a tape strong enough to withstand the necessary winding tensions in making a cable and also rigid enough not to wrinkle when the cable is wound onto the storage drums. Usually one of the polyurethane layers was dyed so that the tapes can be visually monitored during the winding process.

Several laminates using three layers of 25 μm thick polypropylene tape with different polyurethane formulations and dyes were studied. In addition tapes were delaminated so that both dyed and undyed urethane layers could be measured separately. The results showed that the major sources of dielectric loss in the temperature range of 4 to 10 K were the sub 4.2 K loss peak in the original polypropylene, which decreases with increasing temperature and the loss due to the polyurethane which increases with increasing temperature. The tan δ at 100 Hz ranged from 18 to 41 x 10^{-6}, which is somewhat higher overall than the desired value of 20 x 10^{-6}. The only effects that dye had on the loss in these laminates was at temperatures above 150 K.

In addition, several laminates made from two layers of a new 50 μm thick polypropylene film were investigated together with the new polypropylene. These laminates had tan δ of 13-18 x 10^{-6} at 100 Hz in the temperature range of 4 to 10 K. The lower loss of these laminates was established as being due to a reduced urethane content and either less antioxidant or a different type of antioxidant in the polypropylene layers.

Compressibility measurements were made on the laminates in order to predict cable bendability. In addition, the laminates were examined for void content in the urethane layers in order that control of the laminating process could be established to minimize the presence of voids which could serve as a source of electrical discharge.

Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

Oil impregnated paper (cellulose) tape has been for many years one of the most commonly used types of electric insulation in high power AC transmission cables. The current and projected needs for more efficient power transmission systems have elicited considerable interest in the development of oil impregnated or oil filled cables operated at 700 Kv-1000 Kv in which polymer tape insulation will be used instead of the conventional paper tape which is unsuitable because of its large dielectric loss.

In a project, sponsored by Brookhaven National Laboratory with DoE funds, a program has been initiated in the Polymer Science and Standards Division for evaluating the suitability of various types of impregnated AC transmission cables. The goals of this study are: (a) the measurement of the dielectric constant and dielectric loss of candidate films between 273 K and 423 K; (b) the determination of the dependence of the dielectric loss on the fine structural characteristics of the films; and (c) the specification of the dielectrically most suitable type of film for the intended end use.

In FY 1979, the special dielectric cell needed to measure polymer films was tested and modified so that it now gives reproducible loss measurements on polymer films in the temperature range of 300 to 420 K to a resolution in tan δ of 1 x 10^{-6}. In addition, several polymer films were studied in this temperature range at 100 Hz and 1 kHz. The samples were studied as a function of several temperature cycles in order to see if elevated temperatures cause changes in the observed dielectric loss, possibly signaling aging in the polymer itself. The samples studied to date include several of the polypropylene films studied previously at cryogenic temperatures and several new polypropylene films prepared by Battelle Institute for BNL that were extruded, rolled, and drawn from commercial polymers.

The main features found in the dielectric measurements where the presence of a loss peak at about 300 K, and a loss minimum around 350 K followed by rapidly accelerating loss above this temperature up to 423 K which was the highest temperature at which measurements have been made so far. No sign of the α loss peak near 390 K was found. The loss varied appreciably among the different samples studied with minimum tan δ at 353 K of 30×10^{-6} which is a very low value. In addition, mechanical and dielectric instabilities were observed in the Battelle samples.

The Battelle samples are currently undergoing x-ray diffraction and morphological studies to characterize them and comparisons will be made with the heated samples in order to determine the nature of any temperature induced aging which may have occurred.

Porous Polymer Tapes for High Voltage Transmission Cables

A. J. Bur, M. G. Broadhurst, and W. P. Harris

Existing underground high voltage transmission cables are made with an insulation consisting of layers of paper tape saturated with a dielectric oil. This system has proved to be adequate for voltages up to 325 kV. At higher transmission voltages dielectric dispersion in the paper produces unacceptable dielectric losses. In the foreseeable future electrical transmission at voltages higher than 325 kV will be necessary and a substitute for paper is being sought. A polymer material is a logical choice. Some work on solid polymer films has been carried out in the past but the permeation of oil throughout the lapped tapes and encapsulated voids in the films are problems which impede the use of solid films. It is possible that porous polymer tapes can overcome these problems through improved oil permeation and decreased occurrence of unfilled voids.

The Electric Power Research Institute (EPRI) is supporting this porous polymer tape project. The objective of the project is to establish a screening program by which candidate materials can be tested and a judgment made regarding their suitability as cable insulation. The screening program which we have developed consists of criteria for physical properties which the tapes must have and a description of the tests by which these physical properties can be measured. On the test schedule there are 21 tests to measure the following physical properties: dielectric constant, dielectric loss, dielectric breakdown, softening temperature, mechanical moduli in three directions, coefficient of friction, yield strength, fracture strength, solubility, creep and recovery, swelling, and degree of void filling.

With the exception of the degree of void filling and solubility tests, a description of these tests was obtained from literature sources and ASTM test schedules. The degree of void filling and solubility tests have been developed through our own laboratory experience. For these two tests, we have used a method which is designed to measure the buoyant force of a sample immersed in a dielectric oil.

To measure the degree of void filling, the density of a porous sample is first measured in a calibration fluid which is chosen because of its efficient permeation into the material being investigated. (For example, heptane is known to permeate into polyethylene filling microvoids in the material). It is assumed that this calibration fluid fills all pores and voids so that the true material density can be obtained from the buoyant force measurement. A buoyant force measurement is then made for the sample immersed in a dielectric oil. The difference between the true specific volume and the immersed-in-oil specific volume is equal to the specific volume of unfilled pores. Solubility can be measured by weighing the dry sample before and after immersion in the fluid being tested.

Oil permeation into the sample is a common conditioning step in many of the dielectric and mechanical tests which must be carried out in oil. Temperature and vacuum cycling are often necessary in order to increase the permeation of oil and decrease the unfilled void volume. The buoyancy measurements are being developed to observe these conditioning parameters.

Four materials and two oils have been used in these experiments. The materials are a polypropylene synthetic paper (PPSP), a porous polypropylene (PP), a polyethylene synthetic paper (PE) and a paper-polypropylene-paper laminate (PPP). The oils are an alkyl benzene oil and a polybutene oil. The results show a range of void filling from very little for PPSP to complete filling for PP.

A final report for this project has been submitted to EPRI for publication.

Thick Electrode Transducers

A. J. Bur, H. E. Gilpin[1], and M. G. Broadhurst

The fabrication of transducer specimens of PVF_2 with thick, well adhering electrodes was attempted. The objective was to study the influence of the mechanical properties of the electrodes on the PVF_2 transducer behavior. It is expected that the hydrostatic response will be enhanced by a factor of 2 to 3, if the electrodes maintain their own integrity and exert a stress on the polymer film during temperature and/or pressure changes. Up to this time transducers fabricated in our laboratory have had very thin evaporated electrodes, several hundred angstroms thickness. Because the electrode is so thin, the mechanical properties of the polymer substrate dominate.

Metals such as Ni, Au, Ag, and Cu have moduli which are 30 to 40 times larger than that of PVF_2. A metal electrode of 0.4 μm thickness will have the same rigidity as 12 μm of PVF_2. A metal electrode of 4 μm thickness will have 10x the rigidity of the polymer. Relative to the polymer, a thick electrode can be considered rigid so that when the polymer contracts, a stress between electrode and polymer develops. The effect of this stress is to decrease the thickness of the polymer film via Poisson's ratio. The factor which controls this effect is $1 + \nu/1 - \nu$ (ν = Poisson's ratio). For $\nu = 1/2$, this factor is 3, i.e., threefold enhancement of the change in thickness. Correspondingly, there should be a threefold increase in the piezoelectric response.

At this time we have not successfully made a thick electrode specimen. Several approaches have been attempted. Initially the approach which we took was to evaporate 1000 Å Ni electrodes onto PVF_2. The speciman was then poled and its piezo- and pyroelectric coefficients were measured. The speciman was then placed in an electroplating bath and an attempt was made to plate Cu on top of the Ni to a thickness of 3 μm. This plating, however, did not adhere well to the Ni. It either did not plate at all or after plating, flaked off. In spite of the flaking Cu, one apparently intact speciman was measured and found to have the same piezo- and pyroelectric coefficients as before plating. The specimen was observed to be electrically noisy and to have a large background current in the shorted condition, presumably due to ions injected into the polymer from the plating process.

Other attempts at electroplating included Au plating on Ni, electrodeless Ag plating followed by Cu plating; and Au plating on top of Ag spray painted electrodes. In all cases where electroplating was used the specimens became electrically noisy so that in some cases, it was not possible to measure the coefficients. In other cases the Au and Cu plated electrodes flacked off. Although two specimens were measured, no conclusions could be drawn from these data.

Brass shim stock, 25 μm thick, was also used for electrodes. In this case, the brass shim was glued onto an evaporated Ni electrode. No change was observed for the coefficients. It is not known whether or not the adhesion of the brass shim is adequate enough to effectively clamp the PVF_2.

An attempt was made to simulate the mechanical rigidity of a thick metal electrode by placing a speciman in a ring collar which held the speciman fixed at the perimeter of the ring. Measurements on those specimens with the collar in place were found to be approximately 10% higher than those without the collar. It has been suggested that the time scale of the experiment is too slow and these collared specimens relax before the effect can be observed.

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[1] Summer student/guest worker.

A series of specimens with evaporated aluminum electrodes of various thicknesses were prepared. The thickness ranged from 4000 Å to 32,000 Å. Measurements of the piezo- and pyroelectric coefficients showed no significant differences for this series of specimens.

At this time specimens are being prepared with evaporated Ni electrodes at 5000 Å and 10,000 Å thickness. Although these electrodes can not be called "thick", the amount of deposited metal may be enough to produce the expected effect of enhanced response due to electrode rigidity.

ASTM Activities

W. P. Harris

ASTM Committee D-9 met three times in this period:

October 17-19, 1978, in New Orleans
March 19-21, 1979, in Cincinnati
June 18-20, 1979, in Philadelphia

Mr. Harris, Chairman of D-9 and of its Executive Subcommittee, attended and chaired these meetings, and also took part in the activities of several of the subcommittees.

At each meeting 20-30 standards were balloted for revision or reapproval. The Committee had been working hard to bring all its standards into conformity with the "Blue Book" by including a section on sampling as required. However, as a result of a special conference on revision of the "Blue Book" held at ASTM headquarters in Philadelphia in September 1978 (attended by Mr. Harris), it was decided to relax the requirement, as applied to test methods. The revised "Blue Book" is expected to appear in October 1979, with the section on sampling no longer mandatory for test methods. Because of this, D-9 is no longer automatically inserting a sampling section, but is looking at each document to see if such a section would be helpful, or whether reference to standards on sampling can suffice. Committee D-9 has prepared such a general standard, D 3636, "Sampling and Judging Quality of Solid Electrical Insulating Materials," with sampling tables adapted from MILSTD-105D.

During this period the following new standards prepared by D-9 were approved by the Society and issued:

D 3638	"Standard Test Method for Comparative Tracking Index of Electrical Insulating Materials"
D 3755	"Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials Under Direct-Voltage Stress"
D 3756	"Standard Test Method for Evaluation of Resistance to Electrical Diverging Fields"

Mr. Harris attended the Biennial Conference for ASTM Technical Committee officers in Philadelphia in September 1978. Several problems were addressed, including that of getting increased participation in Technical Committees. As a result of this meeting, Headquarters is preparing promotional letters to send to selected lists of prospects. One of the first to be scheduled is one for D-9, to be sent to persons who purchase Parts 39 or 40 of the Book of Standards, but are not members. Mr. Harris participated in the preparation of the letter, and it is now in the process of being printed and sent.

Subcommittee 91 on International Standards continues to be very active. D-9 shared support of several delegates to TC-15's meetings in Zurich, Switzerland, in April 1979.

The new section on Electrical Safety formed last year in the S/C on Electrical Tests has been moved to S/C 94 and broadened to include all aspects of safety during the making of tests on solid electrical insulating materials.

Several new standards are in preparation, and a major revision of one of D-9's most widely-used standards, D-150, is underway.

Space Charge Studies

A. S. DeReggi and M. G. Broadhurst

The thermal pulse method of measuring the distribution of charge or polarization across the thickness of dielectric films continues to be relevant to advancing our understanding of space charge phenomena in polymers and the electrical properties of polymers in general. Evolutionary improvements in the data processing and in the data analysis methodology have been made recently and new results on PVF have been obtained in collaboration with Dr. Sidney Lang of the Ben Gurion University of the Negev (Israel) who was a guest worker at NBS for two months. In addition, survey measurements of charging phenomena in non-polar polymers have begun.

Previous theoretical work at NBS showed that the information which can be obtained unambiguously from thermal pulse data consists of Fourier coefficients of the charge or polarization distribution. However, the diffusive nature of the thermal conduction process results in unfavorable conditions for recovering a large number of Fourier coefficients, particularly if the charge distribution is concentrated at a depth removed from the thermally pulsed surface. To offset this disadvantage, a first-rate data acquisition scheme including signal averaging for the enhancement of the signal-to-noise ratio is required. In addition, carefully programmed numerical computations are needed as part of the data analysis if all the information contained in the data is to be extracted. During the past several months, the existing data acquisition system has been interfaced to an Interdata minicomputer in the Division. Programming to handle the data stream is complete. Programming to extract information about charge and polarization distributions on the Interdata is currently underway. During Sidney Lang's visit and thereafter, curve fitting programs were written and run in the NBS computer to interpret qualitatively new data on PVF in terms of adjustable parameters including the effective depth and width of the polarization. It was confirmed that during the initial stages of poling, polarization first becomes significant towards the poling cathode, in contrast to the situation of PVF_2 where polarization first tends to concentrate towards the poling anode. The two types of behavior strongly suggest effects due to space charge of opposite signs in the two polymers. It was also found that polarization grows and spreads while the poling voltage is progressively increased. This work is currently being prepared for publication. Thermal pulse measurements of a survey nature have also been performed on charged non-polar polymers including polyethylene and polytetrafluoroethylene, which are two commonly used materials in the electrical power industry. Charging was accomplished by subjecting samples for a period of time to an applied voltage at various temperatures. The preliminary results have indicated that charging occurs and that the sign of the charge depends on the electrode material as well as other parameters. Systematic data are being developed for a range of metal/polymer interfaces and for a range of charging voltage and temperature. An attempt is being made to understand the charging data in terms of a simple picture where a polymer can act as a donor or acceptor of electrons depending on the properties on the metal/polymer interface. In the case of 30 μm thick PE charged at 80 °C using a charging voltage of 1750 V and a charging time of 90 minutes, it was found that as the electrode material (anode side/cathode side) was changed from Al/Al, Au/Al, Al/Au, Au/Au the signs and amplitudes of the thermal pulse responses changed. These results suggest that PE was an acceptor relative to Al and a donor relative to Au. Some aspects of this research seem directly pertinent to the insulation problem in electric power cables. In particular, it is relevant to ask whether a particular combination of polymer, or polymer blend, and metal electrode could be found which is resistant to space charge accumulation and hence minimize the space charge enhancement of local fields in the polymer. This space charge enhancement is one probable cause of aging and failure of cable insulation.

Piezoelectric Polymer Fuzing

S. C. Roth, A. S. DeReggi, and S. Edelman

This project is sponsored by the U. S. Army Armament Research and Development Command. It developed from previous work by NBS in cooperation with Frankford Arsenal reported in NBSIR 75-724 (R). NBS is to assist ARRADCOM to determine the feasibility of using piezoelectric polymer film in impact sensors for fuzing applications in several particular geometries.

Two male forms have been built to facilitate mounting an irregularly shaped polymer sensor inside the ogives (forward part of the casing) of selected projectiles. The two forms built so far differ slightly in the length of the forward sections. The machining of the forms was done by numerical control and the directions were preserved on tape so that additional modified forms can be constructed with a minimum of additional design.

Six pre-prototype polymer sensors were designed, constructed, and delivered to ARRADCOM. After some minor modifications and testing at ARRADCOM, they are to be subjected to reverse ballistic tests in an air gun at HDL.

Some preliminary tests have been performed on our drop tester to study the effect of impacts of limited area on the output of large area (several wavelengths) sensors fixed to metal backing.

Structure and Performance of Piezoelectric Polymers

G. T. Davis and M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

Although the best piezoelectric and pyroelectric activity from polymers is still less than that from good ceramic materials, the other properties of polymers often made them the preferred transducer material. Some of tne polymer properties which made them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. The interest in the use of polymeric transducers continues to increase as evidenced by the requests from other government agencies, by the large number of requests for information by mail, phone, and personal visits, and by the 17 papers presented at the American Physical Society meeting in March 1979.

In principle, any polar polymer can be made piezoelectric by preferentially aligning its dipoles in an applied electric field while in the liquid phase, then freezing in the alignment by cooling below the glass transition before removing the electric field. Practical use requires that T_g be greater than ambient temperature but amorphous polymers have other limitations in that the degree of alignment (polarization = net dipole moment/unit volume) is only weakly linear with applied field, and the electric fields that can be applied are limited by rather low electrical breakdown strengths above T_g. The polymer of primary interest continues to be poly(vinylidene fluoride) in which the polarization resides in the crystalline phases of the polymer and the polarization attainable is an order of magnitude larger than that of typical amorphous polymers.

The model developed here for piezoelectric and pyroelectric response from a polymer composed of thin lamellar crystals with preferentially aligned dipoles dispersed in a randomly oriented amorphous matrix was published in J. Appl. Phys. 49, 4992 (1978). Data relating piezoelectric and pyroelectric response to measured polarization using the expressions developed from the model were submitted to ONR as technical report number 11 and have been submitted to the Journal of Applied Physics. The data obtained indicated that the polarization charge was compensated by real charge at the external electrodes rather than at the crystal-liquid interfaces throughout the polymer film. Further evidence for this conclusion was obtained from measurements on a thick (0.13 mm) specimen of PVDF supplied by EMI of Great Britain. The ratio of piezoelectric to pyroelectric response for this sample was about two times larger than usually observed which was traced to the fact that the film had many tiny voids and was therefore more compressible than solid material while thermal expansion properties were unaltered. The enhanced effect of voids could be expected only if the polarization is compensated externally.

A cooperative model has been developed to describe ferroelectric polarization in polyvinylidene fluoride (PVDF). The molecular dipoles within the crystal are assumed to have two or more orientations available to them and the lattice energy of a given orientational site is assumed to be proportional to the fraction of molecules having that orientation. An analytical solution was obtained for the 2-site model which predicts polarization hysteresis typical of ferroelectrics. However, a more complex 6-site model, which can be analyzed numerically was needed to account for observed infrared hysteresis data and electric-field-induced x-ray orientation changes. Although the model is simple, rather complex behavior is observed including a gradual increase or decrease in the remnant polarization with number of cycles of electric field application. Though the agreements with various experimental data are good, an obvious need to include kinetic effects in the model was indicated. These results have been communicated to ONR as technical report number 13 and submitted to the Conference on Electrical Insulation and Dielectric Phenomena.

All the available data indicate that only about 50% of the maximum polarization that can be expected in PVDF has actually been achieved. This is probably due to the incomplete alignment of dipoles in the electric field. A study of the effect of crystal orientation on poling has been initiated using x-ray diffraction. A Phillips diffractometer has been modified so that a polymer film can be oriented at any position in the beam and a transmission scan obtained. The electric-field-induced phase transitions from alpha to the polar alpha phase and then to beta phase which were reported here last year are particularly useful for this investigation. This phase transition from α to polar-α results in the loss of 100 and 120 peaks while increasing the intensity of the 200 peak.

Conversion to the beta phase at still higher fields results in even greater changes in the diffraction peaks. After several unsuccessful attempts to apply high electric-fields to PVDF samples in the alpha phase which were obtained from suppliers in that form, we resorted to melting the mixed phase biaxially oriented films and stretched them at high temperature to obtain uniaxially oriented alpha films. These samples still withstand electric fields in excess of 2 MV/cm.

A fourth crystal form of PVDF has been reported. It is thought to have a tttgtttg' chain conformation and is also thought to crystallize in a polar unit cell. We have confirmed literature reports that annealing through the melting point of alpha phase in the presence of a polymeric surface active agent results in complete conversion to this gamma phase. The poling characteristics of unoriented films of gamma phase PVDF are now being investigated.

An important aspect of piezoelectricity in PVDF which requires much further investigation is the mechanism through which the polymer gradually loses its electrical activity at elevated temperatures. Future work will be directed toward determining the parameters that most affect the thermal stability. The influence of the initial crystal phase on the ultimate stability will be an important part of this study.

Polymer Sensors for NDE of Bearings

S. C. Roth, S. Edelman, J. F. Mayo-Wells[1], and J. M. Kenney

The 1979 NDE work of the Bulk Properties group consisted of a comparison of the usefulness of polymer sensors and conventional accelerometers for monitoring the condition of bearings. The study led to the publication of a paper in the Proceedings of the 28th

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[1] Electron Devices Division, National Bureau of Standards.

Meeting of the Mechanical Failures Prevention Group, NBS Special Publication 547, pp. 303-314, July 1979.

The study used a horizontal shaft supported on ball-bearings, a quiet bearing at one end and a noisy bearing at the other. An isolated electric motor was coupled to the shaft by a flexible belt so that only the bearings contributed measurable noise to the structure supporting the shaft. A polymer sensor was fixed to the stationary race of each bearing and a miniature piezoelectric accelerometer was mounted on the supporting structure as close to each bearing as practicable.

It was found that polymer sensors have several advantages. The principal advantage derives from the flexibility and low density that allow the polymer sensor to be mounted directly to the bearing. So mounted, it responds only to the bearing noises. Conventional accelerometers are relatively massive and require specially prepared mounting surfaces of appreciable area. These characteristics require them to be mounted some distance from the bearing where they can be affected by noise from other sources. The extraneous noise can cause uncertainty as to which of several bearings is bad.

It has been suggested that polymer sensors can provide a non-invasive means for detecting cracks of the kind affecting DC-10 airplanes recently. A polymer gauge cemented to a metal surface responds to surface strain in all directions and detects a signal which can be analyzed into a spectrum of resonances of the metal panel. A change in the structure of the metal preliminary to cracking and certainly development of a crack will cause a significant shift in resonance frequencies and amplitudes. Polymer sensors are inexpensive so that one can be attached to each critical surface. The sensor and lead constitute a continuous thin sheet of polymer that would not affect the behavior of the panel. All resonances of the panel would be excited any time the engines were operating. Before each takeoff, a superposition of the current and initial spectra would detect any change in the integrity of the panel.

Other proposed NDE work consists of the use of polymer sensors to detect broken strands in airplane control cables and the use of polymer sensors in a non-resonant method to measure the real and imaginary parts of the elastic moduli of long, thin rods as continuous functions of frequency and static load.

Polymer Stress Gauge for Intaglio Printing Press

S. C. Roth, J. M. Kenney, A. S. DeReggi, and S. Edelman

This work, which is supported by the Bureau of Engraving and Printing, U. S. Department of the Treasury, involves the development of a gauge to measure the dynamic pressure at critical points in the presses used to print money. It is the continuation of work reported last year.

The first phase of the work was completed this year. The accomplishments of the first phase included measurement of the width of the area of contact between the two cylinders of the press, 18.7 millimeters, the duration of contact of a point on the upper cylinder with the lower cylinder, 0.25 milliseconds, and a qualitative (uncalibrated) determination of the change of the pressure with time during contact. The successful measurement was made with a gauge having an active area two millimeters wide and 14 centimeters long with very narrow inert shoulders. The electrodes were evaporated indium about one micrometer thick. The gauge was mounted directly on the steel cylinder of the upper drum of the press below all of the layers of paper and rubberized canvas used to distribute the printing pressure.

The work of the first phase was described in a report to BEP and in a paper by the authors listed above which was presented to the 10th Annual Symposium of the Paper and Pulp Foundation at Miami University, Oxford, Ohio.

Piezoelectric Polymer Deposition

S. C. Roth, S. Edelman, and M. G. Broadhurst

This project is sponsored by the U. S. Army Research Office. It is a continuation of work described in the previous annual report.

Fused powder films were formed of PVDF-TFE copolymer by fusing a coating of electrostatically-charged, spray-deposited, polymer powder on a metal substrate. Subsequent attempts at poling such films were only marginally successful. Attempts to use the same procedures, which might be expected to give greater piezoelectric activity, resulted in films of uneven appearance, apparently caused by incomplete fusing. Attempts to form smoother films depend on procurement of PVDF powder of low molecular weight.

In order to produce films with better mechanical properties and to pole them so that they exhibit satisfactory piezoelectric activity, it is necessary to have a better understanding of film structure and defects. The mechanical and dielectric properties of fused and incompletely fused films are not well-known. Available experimental data on piezoelectric polymers consists of measurements made on samples prepared in various ways and performed on different samples by a number of different methods under different conditions. The properties of piezoelectric polymers are more dependent on history and treatment than those of crystals and ceramics. As a means of accumulating data which would form the basis of theory to provide the guidance needed for this project, a set of measurements was worked out which yield all of the pertinent mechanical, dielectric, and piezoelectric properties of a polymer sample. The measurements are made in a short time under uniform conditions. The necessary apparatus has been built or assembled, a pair of capacitance bridges has been calibrated and each has been shown to have adequate sensitivity. Apparatus for measuring suitable small displacements by a microphone with a filar micrometer eyepiece illuminated by stroboscopic light synchronized with the motion of the sample has been provided.

Development of Piezoelectric Polymer Stress Gauges for Rock Studies

S. C. Roth and S. Edelman

This work, funded by the Denver Mining Research Center of the Bureau of Mines, is a continuation of work described in the report for last year.

Most of the gauges having single circular active areas were delivered early in this fiscal year. These gauges were similar to those developed for the National Highway Traffic Safety Administration (described in NBSIR 76-1078). Three sizes of active area were built: 5, 3.5, and 1 cm, respectively. These, especially the one centimeter size, have been effective in detecting and measuring the acoustic emission from rock samples under stress. Also, they have been found to survive collapse and crushing of the rock specimens unless a crack develops directly across the active area.

Considerable difficulty was experienced in designing and building the masks for a 16-element array. This has been successfully accomplished; twelve of the arrays have been built; one has been delivered to the Bureau of Mines; and the remainder of the contracted number of gauges will be delivered before the end of the fiscal year. Future work on rock and soil transducers is expected to result from tests on these transducers.

Automated Dielectric Measurements

F. I. Mopsik, S. J. Kryder, and S. C. Roth

The automated dielectric spectrometer is nearing completion. This instrument will record the transient response of a dielectric sample in real time and using numerical transforms automatically determine the dielectric constant and loss of the sample over the frequency range of 10 kHz to 0.001 Hz or below. The instrument should have a resolution of

10^{-5} which is an order of magnitude improvement over most designs. This will allow determination of the dielectric properties of low loss polymers with much greater speed than previously possible.

Work completed in FY 1979 includes a step function generator that can put out simultaneous positive and negative steps of 100 V matched to one part in 10^5 with a 10 μs rise time. This matching is necessary to accurately subtract out the constant capacitance term. A detector has been completed and is being trimmed. This detector will be able to resolve charge changes to 0.1 pC with a 10 μs response time. These and previously completed or obtained components complete the instrumentation.

One other needed piece of support work that has been completed is the development of an efficient numerical Laplace transform technique. The transform gives accurate results over six decades in log time and uses 36 preselected data samples. This performance is quite superior to methods in the literature.

The recording of data for the thermal pulse experiment and the transfer of these data to the Interdata Laboratory computer has been completed and work has started on writing the needed programs for data analysis. When completed this automation will provide a convenient method of determining polarization distributions in polymer films as an aid to studying their piezoelectric and charge transfer properties.

Ultrasonic Hydrophone

A. S. DeReggi, S. C. Roth, J. M. Kenney, and S. Edelman

This project is sponsored by the Bureau of Radiological Health which is also contributing the service of a guest worker. The early work was described in the annual report for last year.

The objective of the project is to develop a piezoelectric polymer hydrophone for characterizing, point-by-point, the acoustic field beamed by ultrasonic transducers such as those used in biomedical equipment. Accurate knowledge of the details of the acoustic field is not otherwise obtainable. The knowledge can be used to ensure both the safety and adequacy of ultrasonic dosage and for research in ultrasonic treatment.

During this year, a number of prototype hydrophones were built and tested at NBS and at the Bureau of Radiological Health. The hydrophone is a taut membrane of polyvinylidene fluoride (PVDF), 50 μm thick, with a piezoelectrically active central spot of about one millimeter diameter. The close impedance match of PVDF to water makes the hydrophone acoustically transparent in use. Thus, whether the hydrophone is held stationary or is scanned across the field, the acoustic impedance presented to the source is essentially the same as it would be if the probe were not present. The response of the probe is flat between 0.5 and 10 MHz. The thickness resonance is about 20 MHz.

The hydrophone was described in a paper presented by the authors listed above and G. Harris of the Bureau of Radiological Health at the joint meeting of the Acoustical Society of America and the Acoustical Society of Japan, November 27-December 1, 1978. J. Acoust. Soc. Am., 64, S.55 (1978).

Plans are currently under way to extend the work to linear arrays, planar arrays to two-dimensional arrays conformed to special shapes such as parabolic dishes. These arrays are of interest in medical imaging systems.

Fabrication of Piezoelectric Polymer Film

A. J. Bur, J. M. Kenney, and M. G. Broadhurst

The Department of the Navy is supporting a project to fabricate piezoelectrically active PVF_2 specimens with thicknesses of 0.81 mm (32 mil). A thick transducer is desired because, relative to the thin film PVF_2 transducers which we have routinely prepared, a thick transducer will have a lower capacitance and a correspondingly higher voltage response for a given strain.

The problem in preparing thick transducer specimens is that the dielectric strength of the specimen is usually lower than that of a thin film of the same material. A commercially available thick film was found to have such a low dielectric strength that the minimum poling field of 800 kV/cm could not be reached. Consequently, we began to prepare thick specimens from PVF_2 powder starting material. The planned fabrication procedure will be: (1) vacuum molding of bubble-free disked shaped specimens; (2) converting the PVF_2 crystal structure from α to β phase by tensile extension or by rolling; (3) evaporating electrodes; (4) poling at 800 kV/cm or higher at 80 °C. At this time, bubble-free disk shaped specimens have been prepared but poling has not been carried out.

POLYMER STANDARDS FOR CONTROL AND EQUITY

L. E. Smith

Task Leader

Molecular weight and molecular weight distributions are the most important determinants of the useful properties of high polymers. They are of primary importance in determining both the processability of the raw materials and the characteristics of the fabricated products. Directly or indirectly, molecular weight is an important part of the specifications used in the commerce involving the tens of millions of tons of plastics produced every year. The ability to determine molecular weight reliably and reproducibly in different laboratories is thus important to both plastics producers and fabricators.

This task has four main technical activities, all aimed at this overall objective of providing a reliable base for the measurement system of molecular properties for use in commerce. First, the current needs of the measurement system used in industry are addressed by projects on the production of standards for molecular weight calibration and research on methods of improving the utilization of gel permeation or size exclusion chromatography which has become a widely used industrial measurement technique. Classical absolute molecular weight determinations are highly labor intensive, which limits the speed of standard reference material production and consumes large amounts of capital per standard. Our highest priority is therefore placed on the development of an absolute molecular weight detector for a gel permeation chromatograph which will be able to produce standards at a much faster rate without a sacrifice in quality. Elastomer SRM's are produced for quality control and specification by the rubber industry. The second technical activity provides the scientific basis for the molecular characterization methods of the future by exploring techniques and theories which meet needs we see growing in the plastics industry. Examples of this are our projects concerned with block copolymers and blends which are rapidly growing segments of total plastics use. The third and fourth activities involve the development and application of molecular characterization methods to particularly critical plastics applications where market forces are not sufficient to attract sufficient industrial effort. Our present work in these activities relates to the use of ultra high molecular weight polyethylene for orthopedic implant use and the development and application of gas permeation measurement methods and standards.

Self-Calibrating Gel Permeation Chromatography

P. H. Verdier

Gel permeation chromatography (GPC) is a widely accepted technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular-weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material, so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape, and in any event is inadequate for quantitative determinations. Some instruments, an example of which is commercially available, attempt to circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required in principle to relate scattering intensity to molecular weight. In addition, qualitative information on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

We are designing and constructing a light-scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle, and which is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of scattering angle and concentration and the results extrapolated to zero scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers.

During the current fiscal year, we have completed construction of a prototype of the scattering cell and its mounting, the two most critical components of the instrument. In the coming fiscal year we expect to complete design and construction of the remainder of the instrument and to begin testing it.

Recycle Gel Permeation Chromatography

F. L. McCrackin and H. L. Wagner

Recycle gel permeation chromatography (GPC, also called size exclusion chromatography) was studied theoretically and experimentally as a method to measure the column spreading parameter and the polydispersity of nearly monodisperse polymer standards. The width of the recycled chromatograms could be accounted for by four causes: (1) the volume of solution injected into the column, (2) the column spreading, (3) the molecular weight distribution of the polymer, and (4) spreading due to the pump. A method was developed to separate the spreading into contributions due to each of the individual causes. Previous analysis of recycled GPC considered the width of the chromatograms as due to only the column spreading and molecular weight distribution of the polymer. By taking the other contributions of the spreading of the chromatograms into account, much more accurate values of the column spreading parameter and polydispersity of the polymer are obtained.

The recycle experiments were carried out with a set of crosslinked polystyrene columns of nominal pore size of 10^3, 10^4, 10^5 and 10^6 Å in a GPC system with a differential refractometer as a detector. The columns were calibrated in tetrahydrofuran and toluene with 5 narrow distribution anionic polystyrenes ranging in molecular weight from 9,000 to 498,000, including SRM 1478 at 36,000 and SRM 705 at 175,000.

To reduce the extent of interference by spurious peaks, which normally occur at high retention volumes after the polymer peak has eluted with distortion of the subsequent recycle peaks, most recent runs were made in toluene. The use of this solvent, together with additional changes in the injection procedure, reduced this interference but did not eliminate it entirely.

Previously, all the various components of spreading were obtained by a least squares fitting of a function of the total spreading to a polynomial in the number of cycles. To improve the precision of the results, we made use of the observation that the spreading due to the injection and the pump was the same for all the samples. These two components of the spreading were then determined separately by measuring the spreading with the columns removed from the chromatograph. Knowing these, it was possible to determine the remaining components, the column spreading and polydispersity, from a least squares fitting of a function of the total spreading to a simple linear relationship in the number of cycles.

Results from this analysis are shown in Table 1. The polydispersities, M_w/M_n of the anionic polystyrenes are quite low, ranging from 1.0027 to 1.09. The spreading due to the columns increases with molecular weight from 0.2 ml at a molecular weight of 10^4 to 0.6 ml at a molecular weight of 2×10^5.

Such measurements now allow the spreading to be measured for any set of columns without using recycle by measuring SRM 750 or 1478.

A chromatogram is obtained for one of these polystyrenes run through the columns, and the spreading due to the columns is then found by subtracting the spreading due to the known polydispersity from the total spreading.

Table 1

Polydispersities and Column Spreading Parameters for Polystyrene Samples

Sample	Solvent	$M \times 10^{-3}$	M_w/M_n	Spreading Parameter, ml
SRM 1477	Toluene	9.1	1.124	0.259
SRM 1477	THF	9.1	1.050	0.158
SRM 1478	Toluene	36	1.0095	0.395
"	"	"	1.0099	0.436
"	"	"	1.0091	0.437
"	THF	"	1.0090	0.394
PC25170	Toluene	51	1.0028	0.336
PC4b	Toluene	111	1.0030	0.581
"	"	"	1.0043	0.449
SRM 705	Toluene	175	1.0062	0.592
"	THF	"	1.0090	0.505
PC50124	Toluene	233	1.0028	0.551
PC3b	Toluene	390	1.0027	0.538

Standard Reference Materials for Rubber and Rubber Compounding

G. W. Bullman and G. B. McKenna

Many of the procedures used by industry for quality control and commercial specifications of rubber depend on standard reference materials (SRM) which are maintained by the Polymer Science and Standards Division. This project renews SRM's as stocks are depleted and produces new SRM's needed by industry for control of processes and commercial specifications which are outside the range of properties available with current SRM's.

The limited resources of the SRM program have prompted us to try to elicit support for an industrial research associate program that would assist in the maintenance of the current program and in the development of new SRM's. Although ASTM Committee D-11 on Rubber and Rubberlike Materials has set up a task group to try to get support for the rubber SRM program from the rubber industry, nothing has been accomplished in this regard since December 1977 and the industry appears content to let the rubber SRM program remain static. In response to this, the Polymer Science and Standards Division has been making efforts to maintain the important SRM's and to eliminate those which are selling at very low levels. The net result will be a streamlined rubber SRM program which serves industry in an efficient manner with materials which are certified by NBS to have certain physical and/or chemical properties rather than having NBS serve as a warehousing distributor for industrial grade materials.

As part of the program to maintain the current important SRM's, we have contracted for the production of a new Butyl Rubber SRM, which will be certified for Mooney Viscosity. In addition, one material, N-t-butyl-2-benzothiozole sulfenamide, a rubber accelerator, will be renewed as an SRM. This material is certified only for homogeneity and fits into the category of warehousing an industrial grade material, but will be renewed to avoid a major disruption in the ASTM standards which rely on this material.

Work within ASTM has also indicated a requirement for a high temperature, high viscosity, Mooney Viscosity reference material. Work will be undertaken to develop such a material during the coming year.

Quasielastic Light Scattering

C. C. Han

Quasielastic light scattering uses the photon correlation technique to measure the two time correlation function of scattered light from polymer solutions. This two time correlation function at any momentum transfer, q, is related to the intermediate scattering function, S(q,t), which in turn is a double Fourier transform of the space and time correlation function of monomer pairs. Therefore, in principle, measurement of S(q,t) can provide not only a measure of the properties associated with the equilibrium distribution of polymer segments such as the radius of gyration, R_G, or the statistical segment length, but also measure physical properties associated with the time evolution of polymer segment distributions, such as the hydrodynamic radius, R_H, or the hydrodynamic interaction strength.

Our most recent efforts have been centered on the development of theories for the intermediate scattering function, S(q,t), and the characteristic frequency, Ω(q), for polymer solutions. Such theories are essential for the interpretation of quasielastic light and neutron scattering data. Our theory includes both temperature and molecular weight dependence specifically. We have also successfully applied this theory to a different characterization technique, intrinsic viscosity.

Interpretation of Scattering Experiments on Polymer Solutions

A. Z. Akcasu[1] and M. Benmouna[1]

Interpretation of dynamic scattering experiments require, ideally, a theory that can predict the intermediate scattering function, S, as a function of t and q, under actual experimental conditions, which are characterized by the temperature and concentration of the solution, and by a chain model consistent with the chemical structure of the polymer. Unfortunately, exact expressions of S(q,t) are available, at present, only for a single unperturbed (θ-condition) gaussian chain without hydrodynamic interaction (Rouse model), or, in the infinite chain limit, with hydrodynamic interaction and preaveraged Oseen tensor (Rouse-Zimm model). In this sense, a complete interpretation of scattering experiments on polymer solutions is an unsolved problem. By using linear response theory, we have been able to express S(q,t) of both linear and circular chains for Rouse and Rouse-Zimm cases for infinite chain limit in a closed form. Also we can express S(q,t) for finite chain lengths of linear chains in the Rouse limit and for circular chains in both Rouse and Rouse-Zimm limits in a closed form. All these can be compared with the method of eigenfunction expansion and the method of solving diffusion equations directly. Advantages of our current scheme have been demonstrated. In the case where an exact solution of S(q,t) can not be obtained, the characteristic frequency, Ω(q), which is the initial slope and defined by

$$\Omega(q) = -\lim_{t \to 0} \frac{dS(q,t)}{dt}$$

can be calculated. The temperature and concentration dependence of Ω(q) in terms of the "blob model" chain statistics can be calculated not only for the intermediate scaling region but also for the upper and lower transition region where information about polymer chain parameters such as radius of gyration, R_G, statistical length, a, and hydrodynamic interaction, B, can be extracted.

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[1] University of Michigan.

Temperature and Molecular Weight Dependence of Polymer Chain Dimensions and Application to Intrinsic Viscosity

A. Z. Akcasu[1]

The molecular, M_w, and temperature, T, dependence of the radius of gyration, R_G, and hydrodynamic radius, R_H, of a polymer in dilute solution have been investigated. Theoretical predictions are compared with experimental results on polystyrene in various solvents as a function of M_w and T, where the lower critical solution temperature is high and has negligible effect [1]. The existing data fell in a region where R_H cannot be represented by a simple power law, $R_H \sim M^{\nu'}$, whereas most of data R_G satisfy $R_G \sim M^{\nu}$. A power law fit to data would yield a $'<$ in this region, even though the theory yields $\nu' < \nu$ in the asymptotic region.

The same molecular weight and temperature dependence has also been successfully applied to intrinsic viscosity [2] using the dynamic argument of Weill and des Cloizeaux. Without any parameters besides the one which has been obtained previously in an R_G measurement, the intrinsic viscosity of polystyrene in various solvents and temperatures can be represented over a range of 5 decades as shown in the Figure 1. This scheme could overcome the difficulty of empirical Mark-Houwink equations $[\eta] = KM^a$, which only apply for limited molecular weight ranges and require a different set of parameters (K and a) for different experimental conditions. Our scheme can be used as a characterization method for polymers with any desired solvent and temperature. Also, it may provide a better universal calibration for gel permeation chromatography.

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(1) "Molecular Weight and Temperature Dependence of Polymer Dimensions in Solution," A. Z. Akcasu and C. C. Han, Macromolecules, 12, 276 (1979).

(2) "Molecular Weight and Temperature Dependence of Intrinsic Viscosity of Polymer Solutions," C. C. Han, Polymer, 20, 1083 (1979).

Our theoretical predictions of $[\eta]/[\eta]_\theta$ through the static argument of Flory-Mandelkern where $[\eta] \sim R_H^3$ and the dynamic argument of Weill-des Cloizeaux where $[\eta] \sim R_G^2 R_H$ are also shown in solid lines. The discrepancy with experimental results of the static argument is due of its failure in differentiating R_G and R_H and in predicting the slower cross-over of R_H from the θ-region to the good solvent limit. The dotted line represents the limiting slope of $[\eta]$ at high M and T.

Single Chain Neutron Scattering in Concentrated Solutions and Melts

A. Z. Akcasu[1], G. C. Summerfield[1], S. N. Jahshan[2], C. Y. Kim[3], and H. Yu[3]

Measurements of the single chain configuration in neutron scattering have always involved taking the limit of small relative concentration of the deuterated polymer. This is done to eliminate interference effects in scattering from different chains. The difficulty with this procedure is, of course, that it emphasizes the least reliable results, namely those from the small relative concentrations of labeled polymers.

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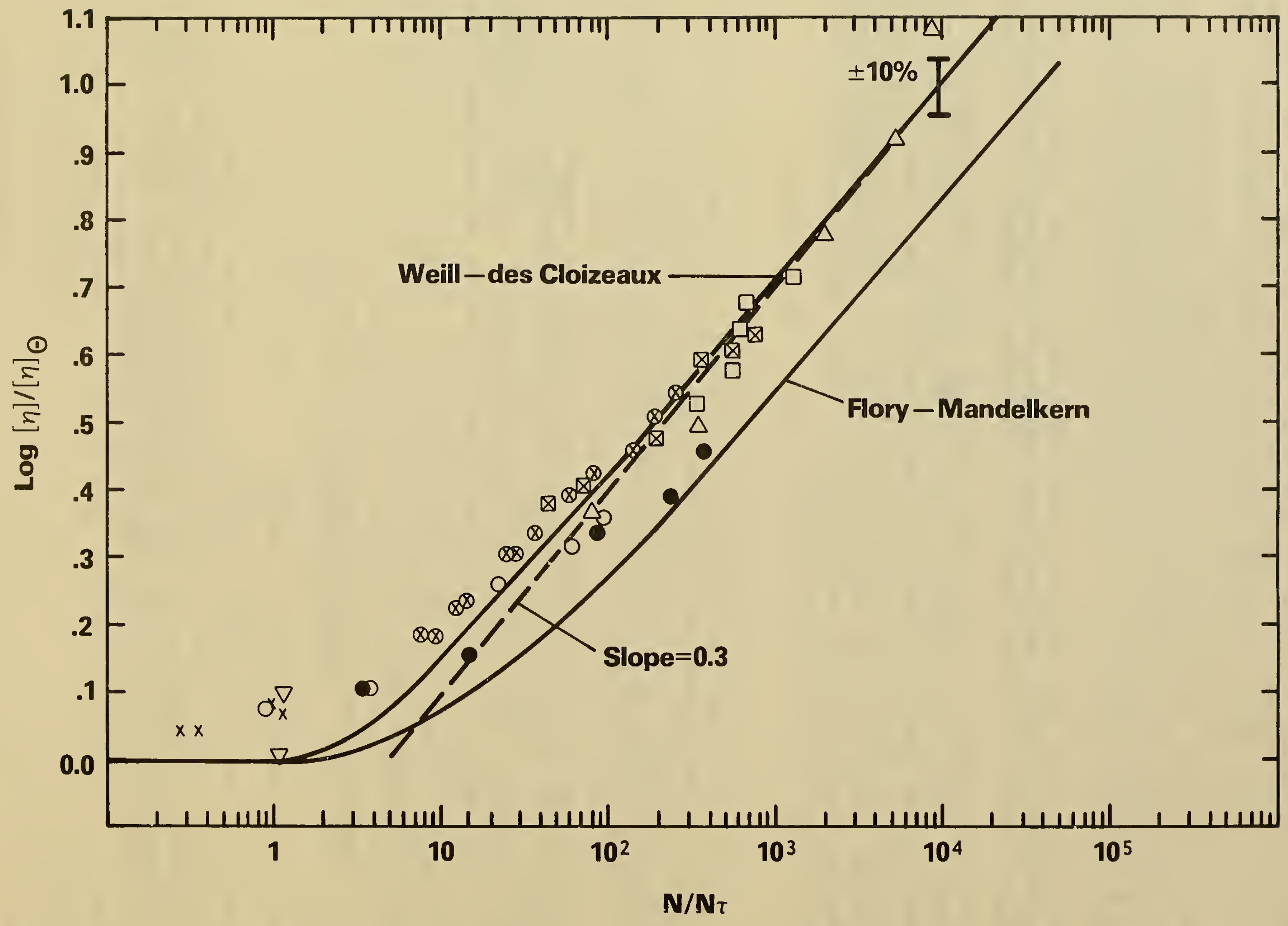

The variation of intrinsic viscosity of polystyrene in various solvents and temperature, with a combined scaling parameter N/N_τ, where $N/N_\tau = M_\tau^2/M_0$ $(n\alpha)$ and $\tau = T-\theta/T$ with M as molecular weight of the polymer, M_0 as the molecular weight of the monomer, τ as the reduced temperature, θ as the theta temperature and $(n\alpha)$ is the only parameter which has been fixed by a different experiment (R_G measurement in our case).

A general method for extracting the single chain scattering function by performing experiments at two different concentrations of labeled chains while keeping the total polymer concentration constant has been developed. This method has been tested experimentally by using 10,000 molecular weight polyisoprene and matched deuterated polyisoprene mixtures. Signal to noise ratios so obtained during 40 hour runs at the NBS facility are excellent and are comparable with results obtained using the D17 instrument in Grenoble, France, with a two dimensional detector.

Characterization of Polymers and Domain Structure Study of Block Copolymers

C. C. Han, D. B. Minor, T. Hashimoto[1], and I. Noda[2]

Characterization of polymers with different architecture such as branched star and comb polymers, and stiff chain polymers will be carried out by small angle neutron scattering. Also, the domain interface structure of linear and star shaped block copolymers will be studied by SANS. Samples and specimens are currently being prepared and characterized by conventional techniques.

Excimer Fluorescence in Dilute Solutions of Block Copolymers

F. W. Wang

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths with respect to the fluorescence spectrum of the isolated molecule. Similarly, excimer formation may take place by intramolecular processes in polymers carrying excimer-forming groups. Thus, excimer fluorescence has been observed in dilute solutions of polymers such as polystyrene, polyvinylnaphthalene, and poly(1-naphthyl methacrylate).

Our experiments [1] as well as those of others [2,3] have shown that in solutions of polymers carrying excimer-forming groups, excimer formation becomes more efficient as the polymers become more compact or as the intermolecular interaction among polymers increases due to aggregation or an increase in concentration. Therefore, excimer fluorescence may serve as a probe for conformational change or aggregation taking place in solution.

We have measured excimer fluorescence in dilute solutions of a polystyrene and of a four-branched block copolymer, each branch of which has a polystyrene block at the free end and a polybutadiene block at the branch point. The solvents used were cyclohexane and a mixed solvent consisting of 5:1 by volume methylene chloride and cyclohexane. As expected, phenyl-group excimer formation for both polymers was found to be more efficient in cyclohexane, a poorer solvent for polystyrene, than in the mixed solvent, a better solvent. But what is more interesting is this: in both solvents, excimer fluorescence was found to be more efficient for the block copolymer than for the homopolymer. These observations suggest that intramolecular or intermolecular aggregation takes place even in the dilute solutions (about 0.03%) of the block copolymer.

Additional experiments will be performed to study the variation of excimer formation with temperature, solvent power, and the number of branches. Experiments based on the fluorescence energy transfer technique are being made to determine whether the aggregation is intermolecular or intramolecular and whether intermingling of the polystyrene block and the polybutadiene block takes place.

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[1] Kyoto University, Japan.
[2] Nagoya University, Japan.

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Fluorescence Energy Transfer Technique for the Study of Polymer Compatibility

F. W. Wang and R. E. Lowry

There has been growing interest in the potential value of reusing scrap plastics as blends of generic mixtures. Because such blends often have very poor mechanical properties, there have been some efforts to develop additives or "compatibilizers" which can improve the properties of the blends. Since a convenient technique is needed to test polymer compatibility, we have initiated a program to evaluate the utility of the fluorescence energy transfer technique for the study of polymer compatibility.

Fluorescence energy transfer can take place between a fluorescence energy donor and a suitable energy acceptor over distances as large as 70 Å. Since the efficiency of transfer depends on the inverse sixth power of the distance between the donor and the acceptor, in a blend containing two polymers labeled with donor and acceptor, respectively, the efficiency of transfer will be small if the two polymers are incompatible and segregated but will be large if they are compatible and form a single phase. Some results of our energy transfer measurements to evaluate the effectiveness of a compatibilizer are described as follows:

Although poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) are incompatible [1], Kwei and co-workers[2] found it possible to render these two methacrylate polymers compatible with the use of poly(vinylidene fluoride) (PVF_2) as "compatibilizer" or a common solvent. We prepared methacrylate polymers labeled with donor or acceptor. The efficiencies of energy transfer in three polymer blends with the following components were determined: 1) donor-labeled poly(ethyl methacrylate) polymer(D-PEMA)/acceptor-labeled poly(methyl methacrylate) polymer(A-PMMA); 2) D-PEMA/A-PMMA/PVF_2; and 3) D-PMMA/ A-PMMA. It was found that, at the compositions studied, the efficiency of energy transfer for the second blend with PVF_2 was close to that for the third which should be homogeneous, while the efficiency for the first blend without PVF_2 was much lower. Thus, in agreement with calorimetry results [2], energy transfer measurements showed that, at some compositions, PVF_2 serves as a compatibilizer for the two methacrylate polymers.

To establish the utility of the fluorescence energy transfer technique for the study of polymer compatibility, we plan to investigate some well understood polymer blends by this technique and compare the results with those from more conventional techniques.

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(2) T. K. Kwei, H. L. Frisch, W. Radigan, and S. Vogel, Macromolecules, 10, 157 (1977).

Statistical Mechanics of a Generalized Lattice Model: A Model for Interacting Polymer Molecules

D. H. Lohse[1] and I. C. Sanchez

We have considered the statistical mechanics of N indistinguishable particles distributed on a lattice of ω sites. The model is a generalization of the usual lattice model in the sense that up to m particles can be accomodated at each lattice site. The potential energy E of the system is assumed to be given by

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[1] NRC-NAC Postdoctoral Associate.

$$E = \sum_{n=0}^{m} \omega_n E_n$$

where ω_n is the number of lattice sites (cells) containing n particles and E_n is the potential energy of a cell containing n particles.

In the thermodynamic limit ($N, \omega \rightarrow \infty$, N/ω constant) the canonical partition function can be evaluated exactly for this model. Some interesting properties of this model include:

1) No first order phase transition is possible.

2) For $m = 1$, or equivalently, $m > 1$, $E_2 = E_2 = \ldots = E_m \rightarrow + \infty$, the free energy is that of a lattice gas without attractive interactions and the distribution law for cell occupancy corresponds to Fermi-Dirac statistics.

3) For $m = N$, $E_n = n\varepsilon$, a Bose-Einstein distribution law is obtained for cell occupancy.

4) For finite $m(m > 2)$ and $E_n = n\varepsilon$ an intermediate distribution law is obtained.

The above assumption that the potential energy of the system is equal to the sum of cell energies is in general invalid for interacting particles. However, there exists a class of intermolecular potentials for which this assumption is correct. This important result is expressed in the following theorem which we state without proof:

Consider a system of N spherical particles of diameter d whose potential energy is pairwise additive. The system is divided into a lattice of ω cells each of volume $(\pi/6)d^3$. A system configuration in which all N sphere centers are at lattice positions is defined as a lattice configuration. Any system configuration can be converted to a lattice configuration by translating all spheres which are located at off-lattice positions to the centers of their respective cells. If the pair potential u(R) between spheres separated by a distance R is proportional to the covolume (the common volume), i.e., if

$$u(R) = \begin{cases} u_o(1 - R/d)^2(1 + R/2d) & R < d \\ 0 & R \geq d \end{cases}$$

then the mean potential energy of the system $\langle E \rangle$ is equal to the mean potential energy of the translated lattice system, $\langle E \rangle_{\text{lattice}}$, with

$$\langle E \rangle_{\text{lattice}} = \omega \langle E_n \rangle$$

$$\langle E_n \rangle = \frac{u_o}{2} \quad \langle n(n - 1) \rangle$$

where E_n is the energy of a cell containing n spheres with $n(n - 1)/2$ pair interactions. A corollary to this theorem is that the mean value of the total covolume is the same in the lattice system as in the non-lattice system. The process of translating the N spheres to their respective cell centers does not alter the mean value of the total covolume. It is this isomorphic property that makes this lattice model so valuable for treating polymer-polymer interactions. The simplest representation of a polymer molecule is that of a spherical particle of uniform (and very low) monomer density. Thus, when two polymer domains overlap the number of intermolecular monomer-monomer interactions will be proprotional to the covolume.

The utilization of this model will enable us to predict the affects of polymer concentration on chain dimensions.

Phase Transition Behavior of the Isolated Polymer Chain

I. C. Sanchez

A mean field theory of chain dimensions has been formulated which is very similar to the van der Waals theory of a fluid. In the limit of infinite chain length, the chain undergoes a Landau type second-order phase transition. At low temperatures the chain is in a condensed state and the mean square gyration radius $<S^2>$ varies $r^{2/3}$ where r is proportional to chain length. At high temperatures the chain is in a gas-like or coil state where $<S^2>$ varies as $r^{6/5}$. In the condensed state fluctuations in $<S^2>$ are very small (or order unity) whereas they are very large (of order r) in the coiled state. A characteristic feature of the theory is that ternary and higher order intramolecular interactions are approximated. At high temperatures only binary interactions are important, but at low temperatures many of the higher order terms contribute. An important conclusion of this study is that a polymer chain does not obey ideal chain statistics at the θ temperature. Although the second virial coefficient vanishes at θ, the third virial coefficient does not; its presence is responsible for the perturbation of the chain statistics. For an infinite chain, θ and the second-order phase transition temperature are identical. When generalized to d-dimensions the theory yields at low temperatures, $<S^2>^{d/2} \sim r$ for all d, and at high temperatures, $<S^2> \sim r^{6/(d+2)}$, and $<S^2> \sim r$, $d > 4$.

Dynamics of Polymer Chains

P. H. Verdier and D. E. Kranbuehl

The dynamical behavior of polymer chains is important for two reasons. First, the principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, non-equilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

Second, the processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end-products. A major shortcoming of present theory is its inability to treat chain entanglements in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

We have previously shown that for our simple chain models, self-entanglement effects lengthen the longest relaxation times of the chains by a factor proportional to about the first power of chain length. However, our models differ from polymer chains in solution in (at least) two obvious respects: the chains are constrained to lie upon a lattice, and motion from one configuration to another is accomplished solely by a series of purely local chain motions. Theoretical work carried out elsewhere appeared to predict a much weaker dependence of the lengthening of relaxation times upon chain length than we had found, leading to the suggestion that our results were artifacts arising from special constraints in the local chain motions we had employed. We subsequently obtained results for chains with modified rules of motion free of these constraints, and showed that the suggestion was incorrect. This work has just been published. During the current fiscal year we have carried out a series of studies of the effects upon relaxation behavior of the type of lattice employed. Preliminary results suggest that self-entanglement effects are somewhat weaker on face-centered and body-centered cubic lattices than on the simple cubic lattices employed in our earlier work, though still much stronger than the current theoretical predictions. We expect to complete this work early next year.

Additional work planned for the coming year will proceed along three lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasi-elastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. Second, as a step in the direction of investigating melt properties, we will extend the simulation studies to non-dilute solutions. Finally, in order to shed further light on the question of lattice-dependence of relaxation behavior, we will attempt limited simulation studies of chains not restricted to a lattice.

Characterization of UHMW Polyethylene for Synthetic Implants

H. L. Wagner and J. E. Dillon[1]

The use of synthetic implants, man-made replacements for body parts, is becoming more widespread every year. Currently, 130,000 implants of Ultra-High Molecular Weight Polyethylene (UHMWPE) are used annually for a wide variety of load-bearing orthopedic prostheses such as hip and knee joints. This is increasing not only because of our growing elderly population, but also because such surgery is being performed more frequently on younger people as the outlook for long-term success becomes brighter.

The main objective of this project is the development of new or modified standard methods for characterizing the molecular weight and molecular weight distribution of UHMWPE. These methods will provide industry with a needed capability for monitoring rigorously the raw UHMWPE used in the manufacture of orthopedic implants. This capability is necessary since the above-mentioned molecular parameters strongly influence both the processing conditions used in the manufacture of the implants, as well as the physical properties (wear, creep, stress cracking) of the products. They will also provide a basis for issuing an NBS reference material for the calibration of instruments used for characterizing the molecular parameters of UHMWPE.

Zero Shear Viscosity of UHMWPE

H. L. Wagner and J. E. Dillon[1]

Previous work has established that single point dilute solution viscosity estimates of the molecular weight of UHMWPE, the basis on which the material is currently sold, are inaccurate. This is due primarily to the previously unrecognized shear rate dependence of the viscosity determination, and the lack of a valid relationship between molecular weight and viscosity (Mark-Houwink relation) for these very high molecular weight materials. In order to provide a meaningful characterization of UHMWPE it is first necessary to determine the limiting viscosity number in the limit of zero shear rate. The zero shear viscosity, an unambiguous quantity, can be the foundation of a rapid and convenient test method at finite rates of shear by polymer producers and implant fabricators alike.

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[1] Food and Drug Administration.

For this purpose, a low shear rotating viscometer of the Zimm-Crothers type has been built. In this viscometer the shear stress is fixed by the magnetic interaction of external electromagnets with an aluminum core set in an inner cylinder. The liquid being measured is kept between the fixed outer cylinder and the inner rotating cylinder suspended in the liquid. The rate of rotation is measured by a counter timer triggered by a laser beam. The entire apparatus is suspended in an oil bath kept at a constant temperature.

In the initial experiments it was found that the precision was inadequate for relative viscosities up to about 1.4, the generally recommended limit for such measurements. In addition, apparent shear rate effects were observed with samples which were known to be shear rate independent. These difficulties turned out to be due in part to the wobble of the rotor and were largely overcome by fabricating the stator and rotor out of uniform bore tubing and by careful fitting of the aluminum core, properly weighted, in the rotor.

Measurements in the modified apparatus at 34.5 °C in cyclohexane and toluene with both a 30,000 and a 12×10^6 molecular weight polystyrene did not reveal any shear dependence at the low shear rates of the rotational viscometer. The high molecular weight polymer did show some shear rate dependence at the much higher shear rates of a variable shear capillary viscometer in toluene and the data were a smooth continuation of the results in the rotational viscometer. Additional runs will be made on higher molecular weight anionic polystyrenes.

These low temperature results, although few in number were satisfactory enough to encourage us to make measurements at 135 °C. At this temperature, however, we find additional modifications are needed because of dimensional changes which occur on heating.

Fractionation of UHMWPE

H. L. Wagner and J. E. Dillon[1]

To determine the molecular weight distribution of UHMWPE, it is necessary to fractionate the polymer because such high molecular weight polymers cannot yet be characterized by chromatography (GPC). Before the advent of GPC, linear polyethylenes with weight average molecular weights up to a few hundred thousand were frequently fractionated by column elution. However this technique becomes more difficult and less efficient as the molecular weight increases and hence was not chosen for the fractionation of UHMWPE.

Instead, the so called "stir fractionation" technique was used. In this method the UHMWPE whole polymer was first dissolved at 145 °C in tetralin. The temperature of the solution was then lowered gradually with fairly rapid stirring until some polymer separated out on the stirrer. This material which separated first is the highest molecular weight fraction. This was removed and the process was continued by lowering the temperature further, removing fractions until no more polymer precipitated.

A total of 7 fractions were obtained between 104 and 90 °C in the first experiment. Viscosity measurements indicated a 4-fold difference in viscosity number (at the same concentration) between the first and last fractions, indicating that at least some fractionation has been achieved. These fractions will also be measured by light scattering and the results should give us an idea of the fractionation efficiency. At this point, the method looks promising.

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[1] Food and Drug Administration.

Development of a Digital Lock-in Light Scattering Photometer

J. R. Maurey, D. B. Minor, and C. C. Han

A state-of-the-art light scattering photometer has been developed for the purpose of measuring the molecular weight of polymer SRM's and ultra-high molecular weight synthetic implant materials. This photometer, which utilizes the principle of photon counting and digital lock in, has been listed with the measurement of previously certified SRM's. Although, further tests are still needed, in our preliminary measurements satisfactory results were obtained down to an angle of $\theta = 15°$ and over a dynamic range of three decades without corrections. It has also shown good long term stability and reproducibility as well as a good dust rejection ratio.

Standards for Gas Transmission Rate Measurements

J. D. Barnes

The documentation of characterization measurements on the polyester film issued as a Standard Reference Material for oxygen gas transmission rate measurements was completed, and the result is available as NBS Special Publication 260-58, "SRM 1470 - A Polyester Film for Oxygen Gas Transmission Measurements."

We continue to assist Committees D-20 (Plastics) and F-2 (Flexible Barrier Materials) of the ASTM in developing improved standards for characterizing the barrier properties of plastic materials. A new standard method presently being balloted, for the coulometric determination of oxygen gas transmission rates references SRM 1470 as its primary calibration standard. NBS is leading a task group formed to revise ASTM D1434, which is the classical method for the manometric and volumetric determination of gas transmission properties. Interlaboratory testing has demonstrated that improved standards are needed before this method can be expected to give reliable results. ASTM task groups working with instrumental methods for water vapor and carbon dioxide transmission rates have received assistance in the statistical design and analysis of interlaboratory evaluations. These efforts may well point out needs for new or improved standards in the form of test methods or reference materials.

A new automated permeation measuring facility is being constructed. The new facility uses a manometric measuring technique, but it has been designed for greater sensitivity (achieved by a cleaner vacuum on the downstream side) and safer operation (achieved by automated safety interlocks to guard against adverse effects from film failures during testing) than our previous system. The new facility is designed to operate above 100 °C, thus enabling us to study glassy polymers at temperatures above and below the glass transition.

A laboratory minicomputer is being interfaced to the facility. Computer control will assist in more frequent monitoring of calibration parameters and in more detailed characterization of the operating temperature and pressure in the system. More complex sequences of experiments, which are needed in studies of glass transition and annealing phenomena, can then be carried out. Transient phenomena, including time lags and desorption effects, are easier to study under computer control. On-line data reduction will prove useful in detecting significant effects that occur during the course of experiments. It was necessary to develop some software to interface the computer with an existing MIDAS controller and to verify that vendor-provided laboratory routines could be used in our application. Software modules for driving the completed facility will be written as needed when construction is complete.

The first project to be undertaken using the new automated permeation measuring facility is a remeasurement of the oxygen gas transmission rate of SRM 1470. This project is being undertaken to ascertain the significance of any drifts in the rates that might result from storage.

The permeance of polymer films to gases is very sensitive to the microstructure of the material, and gases of differing molecular diameters should be useful as probes for determining the size distribution of free volume elements. Earlier work has shown that there are useful correlations between molecular sizes, the state of the polymer, and transport coefficients. We expect to explore these correlations in experiments using several different gases and samples whose thermal and mechanical histories have been varied so as to change the state of the material. Data of this kind can be used to test molecularly-based theories of transport in polymers. This work is also expected to provide a basis for characterizing SRM 1470 for its transmission rate with respect to additional gases, thus allowing this SRM to be more useful in improving the state-of-the-art in transmission measurements. These studies may also result in improved industrial quality control techniques for characterizing barrier materials. Helium gas permeates films much more rapidly than does oxygen or carbon dioxide. If a useful correlation can be found between helium transmission rates and the transmission rates of other gases, it may be possible to use helium in rapid testing to establish whether a process is under control.

The manometric method is useful as a primary standard, but it is inconvenient to use for industrial quality control. For this reason we expect to investigate ways of using gas chromatography in permeation measurements. Such methods would also be useful in research where the permeant stream contains more than one component.

There are a number of problems arising from the use of archaic systems of units in reporting the results of molecular transport measurements. We started work on a modernized set of units, consistent with SI, for describing such measurements. Most problems arise from a failure to recognize that the mole is the appropriate unit for characterizing the amount of substance being transported across a barrier. Using moles per second as the starting point, it is possible to construct units for permeabilities, permeances, and matter currents that are more meaningful than those presently being employed. This procedure has already been followed on the certificate for SRM 1470 and in the new standard method of test for coulometric determination of oxygen gas transmission rate.

Improved Materials for Dissolved Oxygen Measuring Devices

J. D. Barnes

During FY 1978 the Office of Ocean Engineering of the National Oceanic and Atmospheric Administration sought technical assistance from the NBS Polymer Science and Standards Division in improving the precision and accuracy of dissolved oxygen (DO) measuring systems using membrane-type polarographic sensors. The request was predicated on the idea that the polymer membranes being employed to separate the electrochemical cell from the solution to be measured were a possible source of drifts and instabilities in the measured DO values. We could not find support for this premise from an analysis of data presently being collected, which emphasizes the performance of the measuring system taken as a whole.

Our studies were confined to mathematical modelling of the transient response of the sensor to step changes in DO levels or applied voltage. The modelling calculations of the membrane layer and the electrolyte layer could be separated from one another. This requires transient experiments that measure time-lags as well as permeances. The membrane layer and the electrolyte layer are each thought of as slabs in which the transport of oxygen to the polarographic electrode can be treated as a diffusion problem involving a bilayered structure. The time-lag of the composite structure is a fairly complicated function of the time-lags of the separate layers, and the permeance of the composite structure is simply the reciprocal of the sums of the reciprocals of the permeances of the separate layers. It should be possible to devise a fitting algorithm that extracts the time-lags and the permeances from transient responses, particularly if experiments can be performed using step changes in voltage as well as step changes in DO level.

These results have implications for the characterization of inhomogeneous polymer films because they demonstrate that the diffusion coefficients and solubilities determined by sorption experiments should be different from those obtained in permeation experiments on such films and that the inhomogenity must be taken into account in resolving these differences. Further modelling efforts are needed to see if these results can be used as a characterization tool for polymer films with a "skin" whose transport properties are different from those in the "core" of the film.

The modelling work done for NOAA is described in NBSIR 79-1740, "The Influence of Polymer Membrane Properties on the Performance of Dissolved Oxygen Sensors." The results of this modelling study show that parallel measurements of sorption-desorption kinetics and permeation kinetics on films with various microstructures may reveal interesting differences in measured values of transport coefficients. We hope to pursue this problem.

More direct answers to the question of whether aging of polymer membranes cause drifts in DO measuring systems should be obtainable from measurements on membrane materials taken by themselves. A survey of membrane materials being used in DO sensors revealed that polyethylene has been the material of choice. This choice affords a strong electrical signal and a reasonably rapid response, but the high permeability of polyethylene may accelerate certain electrochemical aging processes within the electrodes. The issue of suitable materials for this application needs to be pursued more systematically by separating the membrane component from the electrochemical components of the sensor.

ASTM Activities

J. D. Barnes serves as a member of the Executive Committee of ASTM Committee F-2 (Flexible Barrier Materials) and as Chairman of Subcommittee F2.93 (Statistical Matters). This Subcommittee is responsible for the statistical design and evaluation of interlaboratory evaluation programs for test methods involving flexible barrier materials. Current projects within this Subcommittee include analysis of the results of interlaboratory test programs on bond strengths of laminates, water vapor transmission rates, retained solvents, seal strengths for retortable pouches, and oxygen gas transmission of packages. A workshop on interlaboratory testing, co-sponsored by the Statistical Subcommittee of Committee D-20 on Plastics, will be held in February, 1980. These efforts are aimed at improving the quality of the precision and accuracy statements that ASTM requires in all test methods.

Dr. Barnes also serves as the Chairman of Section F 2.30.01, which is responsible for developing test methods for measuring the barrier properties of flexible barrier materials.

The work of Committee F-2 is closely related to that of Committee D-20. Section D20.70.07 on Gas Transmission properties has task groups on the coulometric method for oxygen gas transmission measurements and on the revision of ASTM D1434, Standard Method of Test for Gas Transmission Rate of Films and Sheets. The introduction of SRM 1470 as a calibration standard has been important in assisting these task groups in their work of improving these methods.

Dr. H. L. Wagner is Chairman of Section D20.70.05, Molecular Weight Parameters. The Recommended Practice for the Measurement of Number Average Molecular Weight by Membrane Osmometry has been approved and will be published in next year's Book of ASTM Standards. The Recommended Practice for the Determination of Weight Average Molecular Weight by Light Scattering has been revised and will be submitted for balloting.

CHEMICAL DURABILITY OF POLYMERS IN USE

L. E. Smith

Task Leader

The growing use of polymeric materials as critical parts in systems vital to national needs such as military aircraft, nuclear reactors, synthetic implants, and solar energy devices demands an improved understanding of the chemical factors controlling the lifetime of such parts. The total economics and safety of many large systems depend on reliable estimates of the lifetime of component materials in actual use. Short-term tests for predicting durability are needed for optimum materials selection, and knowledge of polymer degradation mechanisms is needed to guide the development of protective methods and improve materials performance. This task focuses primarily on polymeric materials used in circumstances where the usual strategy of protective additives is inadequate. For example, effective additives for protection against hydrolytic degradation are not in common use, yet the superior properties of polymers with potential hydrolytic instability make these polymers attractive to designers. Technical activities describe studies of polyester polyurethanes used as elastomers in demanding applications.

Polymers play a major role in solar energy systems which are rapidly growing in importance in the national energy supply. In these devices polymers are exposed to high UV radiation levels but, in many instances, must transmit visible radiation and therefore cannot be protected from photolytically-induced oxidation by the usual methods of opaque coatings or fillers. In spite of this, the economics of the systems demand that the polymers perform satisfactorily for many years. In order to facilitate the implementation of mechanism studies of polymer oxidation, Dr. Brian Dickens spent the period September 1978 to June 1979 as a NATO senior scientist at Le Centre de Recherches sur les Macromolecules, Strasbourg, France. The host scientist was Dr. Jean Marchal who has an international reputation based on his work on radiation-induced polymer oxidation at room temperature.

Oxidation of Polystyrene in Solution

B. Dickens and J. Marchal[1]

Polystyrene is much more inert to oxidation than polypropylene or polyethylene. One way of providing a measurable rate of attack is to use a solvent whose free radical derivatives are active enough to attack the polymer. The radiolytically induced oxidation of polystyrene in $CHCl_3$ and CCl_4 had already been studied to some extent at the CRM. These investigations were extended and parallel investigations were conducted with CH_2Cl_2 and C_6H as solvents. The aims were a) to clarify the differences between the effects of chlorinated and non-chlorinated solvents; b) to study the interplay between radical transfer to the solvent by hydrogen abstraction and intramolecular hydrogen abstraction on the polystyrene molecule; and c) to shed some light on the role of $RO^{\cdot}$ radicals during the oxidation ($RO^{\cdot}$ radicals are formed by the reaction of two $RO_2^{\cdot}$ radicals and can either abstract H or undergo β scission).

The analytical techniques used were gas chromatography, wet chemical analysis, and IR. The amount of ROOH groups formed on the polymer was determined by a colorimetric method developed at CRM. The ROOH groups were then decomposed at room temperature using Cu^{II}/Cu^{I} ions. According to the oxidation mechanism developed at CRM, attack on the secondary hydrogen of PS should lead to benzaldehyde, whereas a repeated attack on adjacent tertiary hydrogens should give acetophenone (both products arising from β-scission of alkoxyl radicals). Attack of one (isolated) tertiary hydrogen gives a chain scission but no small molecule oxidation products are formed. Benzaldehyde and acetophenone were produced in all solutions studied and were detected by GC measurements. The yields of benzaldehyde and acetophenone after decomposition of the ROOH groups by Cu^{II}/Cu^{I} ions were used to show that more secondary hydrogens than tertiary hydrogens are attacked in polystyrene in chlorinated solvents. If this is corrected for the sec:tert ratio of 2:1 in polystyrene, attack in chlorinated solvents is seen to be essentially random along the polymer chains. Intramolecular propagation occurs and is much faster for tertiary hydrogens than for secondary hydrogens. The chain length is governed by the concentration of $RO_2^\cdot$ radicals (which is related to the rate of initiation) and by the probability of transfer to the solvent. At lower rates of initiation more ROOH groups are produced and, in general, more acetophenone than benzaldehyde is formed when the ROOH groups are decomposed by Cu^{II}/Cu^{I} ions. It appears that in this case the kinetic chain lengths are longer and allow more intramolecular propagation to occur.

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[1] CRM, Strasbourg, France.

Intramolecular propagation occurs more in CCl_4 and CH_2Cl_2 than in $CHCl_3$. The H in $CHCl_3$ is notoriously easy to abstract. Those in CH_2Cl_2 are not as active and allow longer chain lengths for the intramolecular propagation. The production of the small molecule oxidation products shows that the alkoxyl radicals, $RO^\cdot$, produce detrimental chain scissions even at room temperature, and their activity is not confined to hydrogen abstraction as is sometimes believed. Protection of the polymer against oxidation may have to consider these radicals as well as the more widely recognized $RO_2^\cdot$ (peroxyl) radicals.

Although the decomposition of ROOH by Cu ions turns out to be less than ideal as an analytical method (because of complexations between Cu ions and $RO^\cdot$ radicals), the results obtained were substantiated by integrated hydrogen absorptions in IR spectra. ^{13}C NMR measurements may be a better way of measuring the site of attack on the polymer backbone although the low sensitivity of this technique requires appreciably oxidated samples.

The amount of attack on polystyrene when C_6H_{12} is used as solvent is much smaller than in the case of chlorinated solvents. The analytical techniques used were not precise enough to give meaningful measurements on these polymers and a mechanistic comparison of the oxidations in chlorinated and hydrocarbon solvents was not possible.

Chemiluminescence from Oxidizing Polymers

R. E. Florin and Brian Dickens

Polymers emit light weakly during oxidation. This effect has aroused recent interest as a means of monitoring oxidative deterioration of polymers. A widely accepted theory of the effect is that the light is emitted during the termination step of the oxidation chain reaction. Although the quantum yield of light emission is very low, estimated at only one photon per 10^9 terminations, this inefficiency can be overcome by the technique of counting individual photons, which leads to an extremely sensitive method, potentially capable of detecting oxidation at temperatures only a little above those of normal service. In contrast, accelerated aging methods require a long extrapolation from test temperatures to service temperatures, over which the mechanism of degradation can change.

The general objective is to obtain a representative data base for correlating chemiluminescence emission rates with overall oxidation rates for polymers of differing physical and chemical characteristics. The appropriate kinetic parameters are the rates of initiation, propagation and termination. We have devised a method for measuring one of the individual rate constants of the process, that of termination. A photoinitiator is added and the sample is exposed to ultraviolet light to reach a steady-state rate of oxidation. The initiating ultraviolet light is suddenly cut off, and the decay of chemiluminescent light emission recorded. A simple second-order termination, such as can be anticipated in a homogeneous rubbery or glassy polymer, should give a linear plot of inverse square root of emission rate against time, from the slope of which the termination rate constant can be computed. To determine the kinetic chain length and the total amount of oxidation, the initiator consumption rate and the steady-state rate of oxygen absorption will also be needed later. Suitable techniques are already well known in the literature.

To conduct automated chemiluminescence experiments of the type described here, a BASIC and a FORTRAN program have been devised. As many as three counting-rate measurements per second can be taken and transmitted to the computer, and the counting interval can be varied in steps during a run. Counting rates significantly above the dark count have been observed for several materials at temperatures of 25 to 50 °C in trial runs. Termination-rate measurements on two rubbers and two glasses are planned.

Further applications of the procedure are: to measure photoinitiation and termination rates, under severe conditions, of clear polymers without additives such as might be used in solar energy equipment; oxidation and chemiluminescence accompanying straining and breaking; and inhibitor efficiency measurements. With more sophisticated mathematical analysis, investigation of heterogeneous materials, semi-crystalline polymers, blends, and filled materials, would also be possible.

Hydrolytic Degradation of Polyester Urethane Elastomers

D. W. Brown, R. E. Lowry, and L. E. Smith

In warm, humid environments the physical properties of polyester urethane elastomers deteriorate more rapidly than expected. This has resulted in premature failure of parts in military aircraft. Under the sponsorship of the Office of Naval Research, we are investigating the degradation, with the goal of developing better methods of predicting the lifetime of these materials.

The observed deterioration has been shown to be due to the acid catalyzed hydrolysis of the polyester component. This decreases the molecular weight and causes changes in physical properties, which have been the basis of lifetime estimates [1,2,3]. We found that some polyester urethanes crystallized on aging, perturbing the effect of the decrease in molecular weight and invalidating the lifetime predictions [4]. Consequently, our effort has been to base lifetime estimates on other changes by correlating changes in acidity, A, with changes in the number average molecular weight, M.

Our results for three commercial polyester urethanes show that A and $\bar{M}^{1}$ increase by equivalent amounts. Their time, t, dependence is given by:

$$A = A_o e^{kt} \text{ and } M^{-1} = M_o^{-1} + A_o(e^{kt}-1)$$

where subscripts denote initial values. Here k, the fractional rate of increase in acidity, is a pseudo first order rate constant. At 100% relative humidity k obeys the Arrhenius equation between 35 and 85 °C and is approximately proprotional to relative humidity. The lifetime of a polyester polyurethane should be estimated by determining k, determining A or M near the limit of use, and solving either of the above equations for t [5]. For use under varying conditions k should be weighted for the fraction of time spent under each condition.

The degradation of polyester urethanes can be retarded by the addition of carbodiimides [6]. These materials function by reacting with the acid present in the polymer[1]. Consequently, the equations above are not valid if carbodiimide is present. We are now trying to develop a method of predicting lifetime in the presence of carbodiimide by following the disappearance of carbodiimide by infrared spectroscopy and the concomitant changes in A and M by titration and gel chromatography respectively.

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Thermal, Oxidative and Hydrolytic Degradation of Polyurethanes by Weight-loss Techniques

J. H. Flynn

This work was undertaken as part of a project whose aim was to determine kinetic mechanisms for the thermal and hydrolytic degradation of polyurethanes and estimate lifetime limits of polyurethane elastomers. Two methylene diphenyl diisocyanate (MDI) polyurethanes, one with polyether, the other with polyester soft segments, have been investigated by constant heating rate thermogravimetry from 10^{-1} to 10^{-4} deg/sec. in vacuum, nitrogen, air, water vapor, and combinations of these atmospheres.

The degradation of the polyether polyurethane was insensitive to the presence of oxygen or water at the high temperatures and fast heating rates typical of commercial TG apparatus. However, at very slow heating rates and temperatures under 200 °C, a low activation energy oxidation reaction was found, precluding the use of high temperature weight-loss techniques for durability prediction in this system. Although water has an effect on the weight-loss of polyester polyurethanes, the kinetics are complex and difficult to interpret. Thus, it appears that thermogravimetric techniques are not a sufficient method of lifetime prediction for polyurethanes, but must be used in conjunction with other types of analysis.

Variable Heating Rate Thermogravimetry

J. H. Flynn

The extrapolation of activation energies from accelerated conditions to service conditions for the purpose of lifetime prediction requires extremely accurate measurements and as modest a temperature range of extrapolation as possible. Weight-loss measurement has been a traditional means of assessing durability as electrobalances are rugged, stable, and accurate.

The kinetics of weight loss of several polymers have been investigated in an apparatus which operates at heating rates in the range from 6 deg/min. to 9 deg/day. The wide range in heating rate results in a broad experimental temperature range within which one is able to accurately calculate parameters and test the constancy of the kinetic process. The slow heating rate experiments reduce the reaction temperatures, thus shortening the length of extrapolation and improving the accuracy of lifetime prediction.

Polystyrene has been investigated in air between 120 and 300 °C and a commercial poly(methyl methacrylate) in nitrogen between 180 and 350 °C. Both of these polymers exhibit uncomplicated kinetic spectra over the entire weight-loss and temperature ranges lending credence to the use of weight-loss techniques for the prediction of their durability.

MIGRATION AND THE DURABILITY OF PLASTICS IN USE

L. E. Smith

Task Leader

All plastic items found in commerce have low molecular weight substances incorporated in them, either as a result of their method of manufacture or from the purposeful incorporation of additives to produce or maintain desirable properties. In use, these substances inevitably diffuse through the polymer to some extent and may eventually migrate out of the polymer.

The consequences of migration are two-fold. First, if the migrating substance is a stabilizing or property enhancing additive, the plastic is left with poorer properties or increased vulnerability to degradation and failure. This is a major failure mode of plastics and programs concerned with polymer durability must explicitly address the possibilities of additive migration. Second, the migrating substance becomes a contaminant of the general environment or, in the case of plastic packaging materials, a contaminant of the material being contained and so questions are raised about the toxicological consequences of such migration. Contamination of food from food packaging materials is regulated by the federal government through the Food and Drug Administration and the control of migrating substances presents an enormous challenge to the scientific basis of regulations.

The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case by case basis, either for selection of materials for optimum durability or for regulation of food and environmental contamination. General material models capable of predicting migration under a variety of service conditions are needed to organize polymer-additive combinations into classes for consideration. The development of these material models is the overall objective of work done in this task.

The technical activities that contribute to this task include (1) the experimental measurement of additive migration by several methods, (2) the compilation of critically evaluated data from this laboratory and the literature, (3) mathematical modeling and empirical correlation of diffusion data for analysis of data and rapid estimation of migration, and (4) fundamental theoretical studies of polymer behavior that can provide truly general predictive models.

Solvent Extraction Methods of Migration Measurement

S. S. Chang, W. J. Pummer, J. R. Maurey, and L. E. Smith

Following the organization of a radiotracer laboratory and a brief exploratory study on the migration of oligomers and other additives of plastics into solvents, a systemmatic program of measuring the migration behavior of small molecules across the polymer/environment interface was undertaken this year. This program is sponsored by the Indirect Food Additive Program of the Bureau of Foods, Food and Drug Administration, and is aimed at developing methods for the more efficient and reasonable regulation of packaging materials in food contact use.

The first phase of the study has been concentrated on polyolefins. During the current year, both linear and branched polyethylene samples were prepared from the stocks of well characterized Standard Reference Materials 1475 and 1476. The additives studied are two ^{14}C-labeled paraffinic hydrocarbons, n-$C_{18}H_{38}$ and n-$C_{32}H_{66}$. The radioactive tracer technique was used in the study for its high sensitivities in being able to detect the presence of nanogram quantities. Qualitatively, the diffusion coefficients for smaller oligomer molecules are greater than the larger molecules as expected from their molecular sizes. Diffusion coefficients are also larger in the branched, less crystalline, samples. Studies now in progress include the modification of individual samples by thermal treatment to achieve variations in crystallinity, and the study of ethylene-propylene copolymers to achieve varied degree of branching as well as crystallinity. Polar antioxidants are also being studied in low and high density polyethylene.

Different solvents were used in the migration studies, including low molecular weight hydrocarbons, the entire composition range of ethanol-water mixtures, food oils, and pure triglycerides. Depending upon the nature of the solvent and the polymer, severe swelling or absorption of solvent may occur. The migration of the additive or oligomer molecules is greatly enhanced by the swelling of the polymer. The simultaneous swelling of the polymer by the solvent and the enhancement of the movement of the migrant produce an apparent non-Fickian behavior of the migration. In a pre-swollen polymer, e.g., polymers presaturated with n-$C_{18}H_{38}$ for the study of exchanging n-$C_{18}H_{38}$ with the surroundings, the diffusion is Fickian. In solvents where the solubility of the migrant is limited, equilibrium partitioning may be reached and the final concentrations can be calculated or estimated from the saturation solubilities. It is also possible under these conditions to measure the uptake of the migrant by the polymer from the solvent phase.

The studies involving food oils and triglycerides as solvents are used to find suitable simulating solvents for food oils. It is found that either triglycerides such as trioctanoin or even ethanol could be considered as food oil simulating solvents for oligomer migration from polyolefins.

Measurement of Migration in Polymers by Inverse Gas Chromatography

G. A. Senich

Inverse phase gas chromatography (IGC) provides a convenient experimental approach for the determination of fundamental material constants which can be used to estimate the extent of migration of low molecular weight materials from polymers into the surroundings. The technique of IGC differs from conventional vapor phase chromatography in that the material of interest, a polymer of negligible vapor pressure, is employed as a stationary phase which sorbs various volatile organic species, often referred to as probes. Processes of solution, adsorption, and diffusion can be studied in relation to various morphological characteristics of polymers such as the degree of crystallinity both above and below glass transition and melting temperatures. The experiment involves injecting a pulse of the volatile solvent into a stream of flowing carrier gas which sweeps the injected substances through a column containing the polymer of interest. At low rates of carrier gas flow the vapor or probe reaches a steady-state distribution between the vapor and polymer phase and the thermodynamics of polymer-solvent or polymer-migrant interaction yield an upper bound to the amount of migration expected. At high carrier gas flow rates the equilibrium state is not approached and the kinetics of polymersolvent interactions can be determined. The diffusion constant of the probe in the polymer can be determined at low probe concentrations and used to estimate the extent of migration over the time period of interest.

A laboratory to carry out IGC studies has been established over the past year. Preliminary IGC results on NBS SRM polyethylene and alkane systems are comparable to literature data. Further studies of the thermodynamic interactions and diffusion behavior of a series of alkane probes with common polyolefins are in progress. These results will be compared with the findings of migration studies conducted by the radioactive tracer method and employed to test and refine models for migration of small molecules in polymers.

Measurement of Antioxidant Migration by Fluorimetry

F. W. Wang

The migration of antioxidants from polymers is being studied by two types of experiments: extraction experiments and concentration profile experiments. In an extraction experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a limited amount of well stirred solvent. Then, the amount of the antioxidant extracted by the solvent is determined at various times by fluorimetry. In a concentration profile experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a large volume of well stirred solvent. The antioxidant concentration profile along the direction normal to the larger surfaces of the sheet is then determined at various times by microfluorimetry, after the sheet is sectioned with a microtome to expose the profile. Comparison of results from the two different measurement methods on the same additive-polymer system will give information on the effects of the extracting solvent on the diffusion and the concentration dependence of the diffusion constant.

Three of the antioxidants which we have examined show room temperature fluorescence sufficiently intense that their migration from polymers may be conveniently studied by fluorimetry. They are N,N'-di-β-naphthyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine (DPPD), and 3-t-butyl-4-hydroxyanisole. We have focused our efforts on the extraction of DPPD from low-density polyethylene. To date, we have developed a procedure to measure the extraction of DPPD from low-density polyethylene. This procedure involves the purification of DPPD, the preparation of polyethylene films which have uniform thickness of about 0.02 cm, and contain DPPD uniformly distributed and undegraded by the preparation, the construction of an extraction device equipped with a cell for making fluorescence measurements without exposing the solution to oxygen, and the preparation of an analytical working curve relating DPPD concentration to fluorescence intensity. This procedure will be used to determine the migration of DPPD from low-density polyethylene to heptane and to ethanol. Concurrently, in collaboration with Dr. R. A. Velapoldi, Center for Analytical Chemistry, we are developing the procedures to perform concentration profile experiments with the use of a microfluorimeter.

A Critical Compilation of Data of the Diffusion of Additives in Polymers

J. H. Flynn

The immediate objective of this project is the compilation of a reliable data base for the prediction of the durability of polymers containing protective additives. With support from the Office of Standard Reference Data, a comprehensive compilation is expected to be ready for publication by the end of FY80.

The scope of the data compilation will be limited to polyolefin polymers. These include high and low density polyethylenes, isotactic and atactic polypropylenes, polyisobutylene, and poly(4-methyl pentene). Carbon-containing migrants -- organics and compounds containing organic radicals -- will be included. Thus far, diffusion constants as a function of temperature and activation energies of diffusion have been computed and compiled for over 200 polymer-migrant combinations. The data compilation is being accompanied with critical annotation giving information on the physical and chemical properties of the migrants and polymers, experimental methods employed, models assumed for the calculation of kinetic parameters, etc.

Thus, the results will serve not only as a data source, but also as a resource from which empirical relationships for estimating diffusion coefficients in polyolefins may be developed and from which sufficient information will be available to test theoretical models for diffusion mechanisms.

An Empirical Formula for Diffusion Coefficients in Polyolefins

F. L. McCrackin

The diffusion coefficients of many materials in polyolefins were fit to the formula

$$D = PM^F$$

where M depends only on the diffusing material and P and F depend only on the polyolefin. The values of M have been tabulated for 21 materials and values of P and F have been tabulated for 7 polyolefins. Diffusion coefficients calculated by this equation agree in general with the measured values within a factor of two, while the measured diffusion coefficients cover four orders of magnitude. The diffusing materials vary from low molecular weight gases to complex antioxidants with molecular weights of several hundred.

While this formula does not predict accurate values for diffusion coefficients, it yields useful estimates when no other means are available. It will also provide a starting point for more comprehensive expressions which will contain parameters with some physical significance to provide a greater predictive capability.

Self Diffusion in Molten Polyethylene

D. H. Reneker, A. Peterlin, and R. Blinc[1]

Measurements of the self diffusion coefficient of molten polyethylene made by a magnetic field gradient nuclear magnetic resonance method were compared with recently reported measurements made by infrared analsis of the change in concentration with time near a boundary between polyethylene and perdeutero-polyethylene. The NMR measurements yield values for the diffusion coefficients which are several times higher than those obtained from the concentration measurement. Further, the values from NMR do not depend upon M_w^2 where M_w is molecular weight.

Analysis of the NMR method indicates that since the nuclear magnetization decays exponentially with a time constant which is approximately proportional to $1/M_w^2$ the NMR result depends most upon the diffusion of material in the low molecular weight tail of the molecular weight distribution. Analysis of the behavior of a polymer with the Schulz distribution indicates that the diffusion coefficient measured by NMR does not depend upon the molecular weight of the sample but is a function of the breadth of the molecular weight distribution. Data from NMR measurements on three well characterized samples with narrow molecular weight distributions show a lower diffusion coefficient for the sample with $M_w = 32,000$ which had the narrowest molecular weight distribution and a higher diffusion coefficient for samples with $M_w = 120,000$ and 13,600, both of which had a broader molecular weight distribution.

Extraction of Additives from Plastics

F. L. McCrackin

Physical models of the diffusion of additives in polymers are needed to provide a basis for the efficient regulation of plastics used in food contact regulations. The rate of diffusion of an additive from a plastic in contact with a liquid is often increased by simultaneous diffusion of the liquid in the plastic, that is, by extraction by the liquid. The diffusion coefficient of the additive depends on both the concentrations of the additive and liquid in the plastic, and the diffusion coefficient of the liquid also depends on the concentrations of both the additive and liquid. This diffusion problem can not be solved analytically, but its solution is required for the modeling of extraction of additives from plastics by foods, as well as for the interpretation of experimental studies of solvent extraction of additives from plastics.

A numerical finite difference method has been developed to solve the diffusion equation for extraction, and a computer program was written. Some initial migration curves have been obtained. The calculated migration curves will first be qualitatively compared with the experimental extraction curves. Later, they will be fit to experimental extraction curves and the results applied to the problem of extraction from plastics containers in use.

Type II Diffusion in Glasses

A. Peterlin

The description of this type of diffusion was applied to spheres and films. The analysis of the experimental observations is in perfect agreement with the predictions of the theory which assumes a constant velocity of the propagation of the glass-gel boundary with the gradual formation of a steady state concentration profile in the glass in front of the boundary. This formation yields a square root of time term in the weight gain while the constant propagation velocity of the glass-gel boundary yields a time proportional term which reflects the linear increase of the swollen gel fraction with time. The geometry of the sphere drastically modifies the time dependence of the weight gain. Together with Professor Sarti, Naples (Italy), one has tried to explain the propagation of the glass-gel boundary by the nucleation effect of the crazing caused by the expansion pressure of the polymer in equilibrium with the diffusant.

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Moisture Absorption and Desorption Effects in Epoxy Matrix Composites

R. J. Rubin

The following conclusions stem from a literature survey of moisture absorption and desorption effects in epoxy matrix composites:

(1) There does not appear to be a significant dependence of durability or performance simply on diffusion coefficients of the epoxy matrix. That is, transient effects associated with diffusion do not appear to be generally important from the point of view of durability although they may be important in accelerated tests. The typical period of exposure of composites to a humid use environment is of sufficiently long duration that the solubility of water in the epoxy matrix is a more dominant parameter.

(2) Absorption and desorption of water associated with ambient variations in the relative humidity is accompanied by dimensional changes in the epoxy matrix and stresses at the epoxy-fiber interface.

(3) Depending upon the nature of the reinforcing fibers, absorbed moisture can concentrate (and attack chemically) the epoxy-fiber interface.

(4) Combination of the stress variations mentioned in (2) with or without chemical attack of the interface mentioned in (3) can result in fatigue-like failure of the composite.

Theoretical methods of attacking the problem of moisture effects in composite failure have been explored. Harlow and Phoenix [1] have made an initial attempt to apply the chain-of-bundles probability model in studying the failure of composite materials, but these authors do not seem to have paid attention to the possibility that the properties of the epoxy matrix, through its absorbed water content, might play a demonstrable role in the model. The emphasis of Harlow and Phoenix lies heavily on the statistical aspects of the problem. Additional useful physical information appears to be available in acoustic emission studies of fiber composite materials [2,3]. This information should provide additional physical inputs to any chain-of-bundles failure model of composites.

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Statistical Thermodynamics of Polymer Solutions

I. C. Sanchez

The lattice fluid theory of solutions has been used to calculate heats and volumes of mixing, lower critical solution temperatures, and the enthalpic and entropic components of the chemical potential. Results of these calculations have been compared with literature data on several polyisobutylene solutions. In most instances agreement with experiment is favorable and comparable to that obtained with the Flory equation of state theory. Several insights into polymer solution behavior have been obtained and include: (1) differences in equation of state properties of the pure components make an unfavorable entropic contribution to the chemical potential that becomes large and dominant as the gas-liquid critical temperature of the solvent is approached; (2) limited miscibility of nonpolar polymer solutions at low and high temperatures is a manifestation of a polymer solution's small combinatorial entropy; and (3) negative heats of mixing in nonpolar polymer solutions are caused by the solvent's tendency to contract when polymer is added.

Theory of Interfacial Tension

C. I. Poser[1] and I. C. Sanchez

A general interfacial tension theory for n-component liquid mixtures of arbitrary molecular weight has been formulated. The theory is based on the lattice fluid model and the so-called "gradient approximation." In the gradient approximation the free energy of a non-uniform fluid is expressed as a sum of a term dependent only on the local density and a square gradient term. The theory has been applied to liquid-vapor interfaces of organic liquids, polymer melts, binary liquid mixtures, and polymer solutions. Currently under study are liquid-liquid interfaces in partially miscible liquids and polymer solutions as well as polymer-polymer interfaces.

Surprisingly accurate predictions have been obtained for pure fluids. For non-polar low molecular weight liquids, the surface tension can be calculated from the triple point to 0.7 of the gas-liquid critical temperature with an error of less than 5% with no adjustable parameters. The theory is somewhat less accurate for polymer melts because it tends to overestimate the surface entropy.

For two-component systems, the lattice fluid theory requires two mixture interaction parameters. These parameters are difficult to determine for polymer solutions and polymer-polymer systems. As a first approximation, we have used the geometric mean approximation to calculate surface tensions for binary systems, except in cases where sufficient data were available to refine the mixture parameters. For low-molecular weight liquid mixtures consisting of non-polar or slightly polar components, the geometric mean rule yields liquid-vapor interfacial tensions as a function of composition which lie within 5% of the experimental data. The theory also correctly predicts the direction of the deviation from ideal behavior. Comparisons of polymer solution surface tensions (calculated using the geometric mean rule) with experiment are hindered by the scarcity of available data. The results obtained are qualitatively correct and in good agreement with experiment for two systems (PDMS-toluene, PIB-heptane). For liquid-liquid systems, the geometric mean approximation must be relaxed. Preliminary studies on such systems are encouraging. For polymer-polymer interfaces, excellent agreement with experimental values can be obtained with reasonable values of the mixing parameters.

Transient Phenomena in the Orientation of the Rigid Spheroids in the Jet Flow

A. Peterlin

In the jet flow the orientation of the rigid spheroids is a one-dimensional problem. Its time dependence can be expressed by a sum of terms exponentially dependent on λ_{2p} Dt where the λ_{2p} are the eigenvalues of the spacial distribution function of the symmetry axis of the spheroids. The time dependent averages of $\cos^2\theta$ and $\cos^4\theta$ determine the intrinsic optical birefringence and the light scattering of such a suspension.

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[1] Guest Worker.

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE

B. M. Fanconi

Task Leader

Current trends are to use polymeric materials in applications where long term performance in the use environment without adverse deterioration of mechanical properties is critically important. An example is the increasing use of plastics and composites in automobiles to achieve lighter weight, more fuel efficient, vehicles. The lack of adequate test methods and data for evaluating long term mechanical performance may result in overdesign which not only leads to more expensive items, but also limits potential weight savings. The NBS has established joint programs on mechanical durability with other federal agencies which are fostering the use of polymeric materials in applications with implications in areas of national concern - health, safety and energy. A joint program with the Department of Transportation concerns the reuse of polyethylene shipping containers for hazardous materials transportation. The program addresses questions about long-term mechanical integrity, especially with ladings which may be even mild stress cracking agents. As part of the National Heart Program, the NIH supports development of accelerated test methods for the fatigue life of biocompatible elastomers which are used as bladders in circulatory assist devices. The Department of Energy supports development of methods to evaluate high temperature, chemically inert, elastomers which are used as seals in geothermal energy production. In all of the above applications, there exists a need for test methods and standards to ascertain the physical limits of polymeric materials in various use environments. Evaluation and control of materials parameters which affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life and environment.

The objectives of the task are to identify and analyze the principal failure mechanisms in polyethylene and elastomers under mechanical stress in the use environment. An integral part of these objectives is to determine relationships between microstructure, mechanical properties, and mechanisms at the molecular level which affect mechanical durability. To reach the objectives requires an interdisciplinary approach combining competences in mechanical properties measurements, fracture mechanics, continuum mechanics, chemistry and physics of molecular processes, spectroscopic techniques of infrared, Raman and nuclear magnetic resonance, x-ray scattering, and electron and optical microscopy. This year we have developed the capability for time resolved x-ray diffraction which shows promise for investigating relationships between microstructure and mechanical properties.

Spectroscopic Investigations of Failure Mechanisms in Mechanically Deformed Polyethylene

B. M. Fanconi, J. P. Colson, and K. L. DeVries[1]

Knowledge of the molecular mechanisms associated with deformation and fracture in polymers provides the basis for predicting long term performance from short time tests as well as insights into how the molecular composition may be changed to improve performance.

The molecular mechanisms associated with mechanical deformation and fracture in polyethylene are elucidated through comparisons between Fourier transform infrared (FTIR) spectra of undeformed and fractured specimens. Small variations in the concentrations of carbon-carbon double bonds, methyl groups, and carbonyl groups result from rupture of carbon-carbon backbone bonds and subsequent free radical reactions. These concentration changes can be detected in difference spectra obtained through subtraction of the digital FTIR data. The detectability of small concentration variations is enhanced by the superior sensitivity of the FTIR method over conventional dispersive infrared spectroscopy.

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[1] University of Utah

The difficulties inherent in comparing spectra of unoriented (undrawn) and oriented polyethylene which plagued previous infrared studies of deformed and fractured polymers have been overcome by preparing specimens for infrared analyses by casting films of the drawn and fractured material, or of the reference polyethylene from solution or the melt. The most apparent discrepancy between our results and those reported previously involves the direction of the change in the number of carbonyl groups. We find that the number of carbonyl groups decreases during fracture rather than increases as determined previously. This result was obtained in films of fractured polyethylene which had been prepared by melt casting as well as solution casting. On specimens taken from regions of deformed polyethylene which did not include the fracture surface we find that the decrease in the number of carbonyl groups is less than when the specimens include the fracture surfaces.

We propose that the decrease in carbonyl groups in fractured polyethylene samples result from preferential backbone bond rupture occurring near carbonyl groups. Subsequent chemical reactions produce low molecular weight ketones which are volatilized during preparation of the films for infrared analysis. Experiments are in progress to substantiate these results on drawn polyethylenes to determine whether a relationship exists between level of deformation and decrease in the number of carbonyl groups.

Mechanical Durability of Polyethylene Shipping Containers

J. M. Crissman, L. J. Zapas, and G. M. Martin

This report summarizes research in the area of performance of polymeric materials used in the manufacture of large shipping containers for hazardous materials transport, work supported by the U.S. Department of Transportation Office of Hazardous Materials Research. A primary goal of this work has been the development of test methods for evaluating stress-crack resistance of ethylene plastics and degree of crosslinking in rotational molded polyethylene containers.

During the past year, studies concerned with stress-crack behavior were expanded to include a variety of biaxial deformation histories such as equibiaxial under inflation, bottle inflation, and bent strip geometries. One important result of this work is the observation that each type of deformation examined, including earlier work on uniaxial creep, yields essentially the same information with regard to stress-crack behavior. On the basis of preliminary data, a new test method employing bent strip geometry has been proposed for evaluating the stress-crack resistance of ethylene plastics. The new test has several advantages over the most common test in current use in that the bend geometry is well defined and controlled and the specimen is subjected to a constant applied load. A test of this type also has the advantage that it can be controlled in such a manner as to optimize testing time.

Also during the past year a wholly new area of study was initiated which is concerned with cross-linkable polyethylenes for rotational molding. This class of materials is now entering the marketplace in the form of large rotationally molded containers for the transport of hazardous materials. The rotational molding of cross-linkable polyethylene represents a different approach to container fabrication than that employed with conventional uncross-linked polyethylenes. For cross-linkable polyethylenes, the physical properties of the final product are highly contingent upon the processing, in particular the cross-linking step. Properties such as impact strength, fracture toughness, and stress-crack resistance are expected to depend rather critically upon the extent of cross-linking. Since the degree of cross-linking clearly represents a key parameter in determining performance, test methods need to be developed which can directly correlate the two. Three types of tests are currently under investigation: stress-crack resistance, swell ratio, and high temperature tensile modulus.

Stress-crack resistance as a function of the degree of cross-linking is currently under investigation, but the work is not yet far enough along to report on here.

A swell ratio test based on dimensional changes alone has been examined for a number of polyethylene samples having widely different degrees of cross-linking and compared to the swell ratio as determined by the conventional ASTM method. A high degree of linear correlation has been established between the two methods and it has been found that both methods yield the same information. The primary advantage of the method based on dimensional changes is that it requires only half the time to perform.

Measurements of the tensile modulus at high temperature carried out on specimens of cross-linked polyethylene having widely different degrees of cross-linking reveal that this method is rather insensitive to the degree of cross-linking achieved and appears impractical as a test method.

Physical Testing of Polymers for Use in Circulatory Assist Devices

R. W. Penn, G. B. McKenna, G. W. Bullman, and F. A. Khoury

This report presents results obtained during the past year in a research program on Physical Testing of Polymers for Use in Circulatory Assist Devices carried out at the National Bureau of Standards with the support of the National Heart, Lung, and Blood Institute of the National Institutes of Health. The main objectives of the program are to develop test procedures for evaluating candidate materials for use in circulatory assist devices (CAD).

The initial phase of our program had been limited by the unavailability of suitable test samples of biocompatible elastomers. To compensate for the lack of biocompatible elastomer samples, we used the standard butyl rubber for samples and we prepared and distributed this material to other investigators engaged in the Physical Testing program. We recently have received several square feet of "Hexsyn" biocompatible polyolefin rubber from Dr. McMillin of Monsanto Research Corporation and a small quantity of "Biomer" polyurethane from Dr. John Kardos of Washington University. Also, we have received approximately thirty square feet of "Avcothane" urethane-silicone copolymer which we have distributed to the other investigators.

Testing of all of these materials has been initiated. We have completed preliminary stress-strain testing of all of the materials. Creep to failure tests are proceeding in both uniaxial and biaxial loading. Uniaxial fatigue tests using sinusoidal loading of the two carbon black filled elastomers have shown a dependence of sample lifetime on frequency which falls between that predicted by stress dependent additive damage and that which would be observed if failure occurred after a constant number of cycles, i.e., "cycles dependent" fatigue. It will be of interest to check this result for the elastomers not filled with carbon black.

Two biaxial fatigue test machines with six testing stations each have been assembled. These devices use pressure controlled pulses of air to inflate circular discs of the test materials at a rate of 3Hz. The pulses are controlled by motor-driven reciprocating spool valves. One of the machines is mounted in a thermostatic bath suitable for testing at temperatures up to about 60 °C. The other is maintained at room temperature. Means have been found to prevent the evaporation of the saline solution in which the samples are immersed and thus to permit constant pressure amplitude testing over periods of several months.

Studies of the fracture surfaces of failed specimens are continuing. The carbon black filled butyl and polyolefin rubbers appear to fail by a crack growth mechanism. The cracks appear to initiate in the interior of the rubber samples, probably at carbon black aggregates. Failure of the butyl rubber samples is detected when a small crack grows through the sample thickness. The polyolefin rubbers fail by a much more rapidly growing crack which extends most of the way across the specimen.

Examination of the urethane-silicone elastomer under the optical microscope clearly reveals that the structure of these membranes is not homogeneous. It has been established that lenticular regions (which exhibit an essentially circular profile when viewed along the membrane normal and which have an elliptical profile when viewed parallel to the plane of the membrane) occur throughout the new test membranes. The diameter of these lenticular regions varies from a few micrometers to several dozen micrometers. The existence of the regions points to the occurrence of phase separation on a gross scale during the casting of the membranes. It is still not clear whether mechanical failure in these membranes occurs preferentially at interphase boundaries.

Fundamental Aspects of the Crystallization, Fine Structure, Deformation and Orientation of Polymers

F. A. Khoury and L. H. Bolz

Activity in this broad category has been limited to two areas. Our efforts have been primarily devoted during the past year to a study of the habits exhibited by chain-folded polyethylene crystals grown from dilute solutions at elevated temperatures from poor solvents. A main initial objective of this investigation was to seek appropriate solvents, from which polyethylene crystals can be grown at temperatures which approach, and if possible overlap, the temperature range (∿ 118 °C - 130 °C) in which the polymer can be crystallized isothermally from the molten state. There have been numerous studies on the habits of solution grown polyethylene crystals in the past. There is, however, relatively little knowledge on the nature of crystals grown above ∿ 100 °C. Our original premise, which current results bear out, was that such crystals would serve as useful models for crystal lamellae grown from the melt. The latter lamellae are usually organized in spherulitic arrays and are consequently much less accessible or amenable to the determination of their lateral growth habits (lateral faceting), their conformations (hollow pyramidal, tent-like, or variously curved), and various details of the molecular organization in them (e.g., fold staggering, tilt of chain stems relative to fold surface). The determination of these features, and others, is essential not only to an understanding of the relationships between mechanisms of crystallization and fine structure at the molecular level, but also to the determination of aspects of the mechanisms of polymer deformation and orientation.

Secondly, as part of an on-going study of the stress cracking characteristics of polyethylene (Crissman and Zapas) we have recently started an investigation of the morphological changes caused in sheets of the polymer when they are subjected to equibiaxial stresses. Information derived from this study will also have a bearing on aspects of the mechanisms of deformation and orientation which underlie compressive stressing as well as biaxial orientation processes used in the manufacture of polyethylene products (e.g., films, containers).

Some initial results are summarized below:

The Habits of Polyethylene Crystals Grown from Dilute Solutions in Poor Solvents:

Linear polyethylene fractions (M.wt. 11400-100500) and ultra high molecular weight polyethylene (UHMWPE, M.wt. ∿ 4.5 x 10^6) have been crystallized from 0.01% solutions in the range 95 °C - 115 °C. Heptyl acetate, heptyl acetate/xylene mixtures, and dodecanol were among the solvents used. Not unexpectedly all the lamellar crystals grown in that temperature range exhibited preferential growth parallel to the b-axis, and at the lower temperatures the lamellae exhibited {110} and (200) lateral faceting. In addition, the axial ratio B/A* increased with increasing crystallization temperature. Interestingly, however, we have encountered instances in which the lateral habits of the lamellae tended to become less well defined the higher the crystallization temperature. In particular, crystal lamellae of the lowest molecular weight fraction (M.wt. = 11400) grown at 115 °C from dodecanol exhibited a lenticular lateral profile (axial ratio 5-6). Although these lamellae were bound at opposite tips by {110} facets the long lateral edges of the crystals were distinctly curved. Whether this later feature is associated with the manifestation of isothermal thickening during the growth of the crystals remains to be determined. A main feature of interest in these crystals is that the chain stems are tilted (34°) relative to the fold surfaces and that the sense of tilt is the same throughout each lamella although there are indications that the magnitude of the tilt may be smaller in the outer lateral regions of the crystals. This later feature suggests that these crystals may possess, in the as-grown state, a slightly S-shaped cross-section when viewed along the b-axis. Evidence that the constituent lamellae in banded polyethylene spherulites grown from the melt possess an S-shaped cross-section has been recently reported in the literature. Details of the stem tilt in these lamellae are difficult to establish. Our observations on the lenticular crystals grown from dodecanol suggest that the stems in lamellae in spherulites may also all be tilted in the same direction relative to the surfaces of the lamellae.

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*Axial ratio B/A = length of lamella parallel to b-axis/length of lamellae parallel to a-axis.

Equibiaxial Deformation of Polyethylene:

A study of the morphological changes which occur when sheets of polyethylene are subjected to equibiaxial deformation has been started. Replicas have been made of the surfaces of sheets which were subjected to overall strains of up to 10%. Examination of the replicas under the optical microscope revealed cracks in the regions of maximum strain (polar region of bubble), which cracks were bridged by fibrils. The lengths of the cracks varied. The most dominant crack (which exhibited a meandering path) was 0.1 mm long and ~ 20 μm wide. Most cracks were of the order of 50 μm long or less. In addition to these clearly distinguishable cracks, available evidence indicates the occurrence of preferential small scale deformation at interspherulite boundaries in the regions of maximum strain. These observations clearly emphasize the lack of homogeneous biaxial deformation under equibiaxial stressing even at strains of 10%.

Characterization of Polymeric Solids by ^{13}C Nuclear Magnetic Resonance

D. L. VanderHart and S. J. Kryder

NMR has traditionally been used to probe the spectral density of molecular motions in polymers. Relaxation times have been used to infer such information. The ability to resolve individual carbon resonances by means of magic angle sample spinning (MASS) in polymer systems has opened up possibilities for measuring relaxation times for each of the carbon sites, thereby gaining information about backbone motions as opposed to sidechain motions. Such distinctions are necessary if one wishes to interpret these motions as being relevant to a macroscopic property such as modulus.

The ^{13}C methods offer advantages over proton methods, particularly in that the observed ^{13}C relaxation time is the superposition of the relaxation times of individual carbons in the sample. Proton relaxation, on the other hand, is usually the result of locally averaged relaxation since the proton spins strongly couple to one another and do not relax individually.

The rotating frame ^{13}C relaxation time, $T_{1\rho}^{C}$, is the easiest relaxation time to measure in polymers; furthermore, if $T_{1\rho}^{C}$ is determined by molecular motion, it will give information about the spectral density of motions in the mid-kilohertz range, an important range for dissipating impact energy. Work done in our laboratory this year has led to a much better understanding of when $T_{1\rho}^{C}$ can be interpreted in terms of molecular motion and when it should not be interpreted this way. It has also led to insights into ways of optimizing experimental parameters for obtaining information about molecular motion.

Investigation of Ultimate Resolution in Solid Polymers by Magic Angle Sample Spinning:

Experimentally, it is found that at 15 MHz frequency for ^{13}C nuclei, crystalline substances and polymers in particular, have linewidths ranging from 2-20 Hz. Furthermore, materials with less order and more molecular motion, e.g., glassy polymers, exhibit linewidths typically in the range of 30-100 Hz. It is clear that the utility of the MASS technique will often be related to one's ability to resolve resonances. For example, if one wishes to evaluate cross-link density in a polyolefin, and if the cross-link involves a tetrahedrally bonded carbon, then the width of the backbone resonances which are also tetrahedral carbons is critical since a wide, intense backbone resonance will very likely obscure a weak resonance close by.

Furthermore, through this work and the work of others, it is becoming clear that chemical shifts observed in MASS experiments are often sensitive to conformational differences. Thus, it was found that the non-crystalline resonance of linear polyethylene is shifted from its crystalline resonance because of the non-zero average gauche content of a non-crystalline chain.

Other effects on linewidth have also been investigated such as the effects of molecular motion and off-resonance proton decoupling. The relative importance of various linebroadening mechanisms varies from sample to sample, especially for polymers. Only if molecular motion is an important linebroadening mechanism will resolution improve at higher magnetic fields. Otherwise, it may even deteriorate. Even so, much remains to be understood about resolution, and from the latest results, it looks like the largest contribution to linewidth is chemical shift dispersion. If this is true, it is possible that improved resolution could be obtained by modifying sample preparation techniques. Nevertheless, it is safe to say that resolution in solids will not be as good as resolution in liquids, in fact, resolution will probably be worse by one to two orders of magnitude. This is an important perspective to have gained in using the ^{13}C MASS technique for studying polymers. For example, this severely limits aspirations for studying tacticity in the solid state.

Orientation and mobility of the non-crystalline regions of linear polyethylene (LPE) and their relationship to modulus:

Non-spinning ^{13}C spectra of chemically simple materials like linear polyethylene allow one to get information about orientation. Furthermore, selection of resonances based on molecular mobility allow one to distinguish crystalline from non-crystalline (NC) material. In particular, the orientation in the NC region was studied as a function of annealing in a cold drawn sample of LPE. The change in spectral features accompanying the decrease in modulus (the latter measured by John Crissman on similar samples) suggested that the number of tie chains decreased with increased annealing temperature.

Infrared Vibrational Analysis of Conformational Disorder in Crystalline Polyethylene

D. H. Reneker, J. Mazur, and J. P. Colson

The infrared spectrum of polyethylene in which 5% of the carbon atoms are doubly deuterated contains bands which are attributed to trans-trans (tt) and trans-gauche (tg) dihedral angle sequences. Experimental observations show that even in crystalline polyethylene there are tg sequences and that the number of sequences as measured by the intensity of the infrared bond increases in the temperature range between 60 and 120 °C.

The tg sequences are presumed to be in folds and other crystalline defects such as point dislocations. Calculations of the conformations of such defects show that the crystalline constraints result in dihedral angles which vary over a wide range of values centered around trans and around gauche. Calculations of the vibrational spectrum for different fold and defect conformations show that the tt band is essentially unaffected by the variations in the dihedral angles which adjoin the tt pair. However, the tg band is considerably broadened since its characteristic frequency is shown to depend on the conformation of the dihedral angles which adjoin it.

The determination of an appropriate baseline for measuring the area under the tg and tt bands is a source of considerable uncertainty. Two choices for the baseline were examined. Both of them showed that the tg intensity increased with temperature. One choice, a baseline fitted to the minima and shoulders of the spectrum resulted in a baseline position and shape that varied with temperature. The other choice established a temperature independent baseline by extrapolating to low temperature the parameters in the temperature dependent baselines. This second choice resulted in a ratio of the area under the tg band which is commensurate with the number of tg sequences expected from x-ray and Raman measurements of the number of folds and point dislocations in the sample.

Investigation of Disorder in Polymethylene Chains

J. Mazur and B. M. Fanconi

Recent work on Raman active longitudinal acoustic modes (LAM) in n-alkanes and polyethylene has demonstrated that these vibrations could be used to determine aspects of the chain conformation of polymethylene chains including the energy difference between gauche and trans conformations. To fully utilize vibrational analyses of LAM for this purpose we have determined the effect of chain disorder on the frequencies and have substantiated the validity of a previously proposed method of calculating vibrational intensities from normal coordinate displacements. We have calculated the Raman spectra of liquid n-alkanes in the LAM frequency range. These theoretical spectra have been used to determine the energy difference between gauche and trans rotational isomers in polymethylenes from analysis of melt phase n-alkane spectra.

In the course of these investigations we have elucidated a previously unresolved aspect of the Raman spectra of n-alkanes by showing that the anomalous band profiles observed in the LAM spectra of some n-alkanes result from Fermi-type resonance between LAM and transverse acoustic modes, the latter of which have little Raman intensity in the absence of this resonance. Our calculations have yielded both the frequency shifts and intensity profiles resulting from these interactions. The intensity calculations were carried out using a method previously developed for LAM intensities of disordered chains. Our analysis provided a means of testing the intensity calculation method and the excellent agreement found indicated that the method is reasonable.

Transport Properties of Drawn Low Density PE

R. Russo[1], F. de Candia[1], V. Vittoria[1], and A. Peterlin

The drawing reduces the sorption and much more the zero concentration diffusivity, but increases the concentration dependence of the diffusivity. Annealing reduces these effects of drawing drastically and brings the transport properties of the sample almost back to the values before drawing. If, however, the annealing is performed with fixed ends the annealed material upon standing at room temperature returns, as far as the transport properties are concerned, back to the values before the annealing. Such an effect can be explained by slow crystallization of the tie molecules which became partially relaxed during the annealing but as a consequence of the fixation of the ends of the sample could not pull back the blocks they are anchored in toward their initial position. After crystallization they form long-range axial connectors which are the main cause of the high axial elastic modulus. If the annealing is performed with free ends, the sample shrinks as a consequence of the contraction of tie molecules. After the shrinkage connects the blocks over a much shorter distance they do not, even after partial crystallization, act as long-range connectors.

Permeation Performance of Polyethylenes Used in Containers for Hazardous Materials Transportation

J. C. Phillips

This project is concerned with developing test methods to be used by the Department of Transportation in formulating regulations concerning the barrier properties of polyethylene shipping containers. Efforts for the current year are concerned with determining the range of applicability of the permachor concept of predicting permeation behavior.

Weight loss determinations were performed at $t = 50$ °C for a n-carboxylic ester series and a n-alcohol series. The ester series consisted of ethyl acetate, butyl acetate, and amyl acetate. The alcohol series consisted of methyl, ethyl, propyl, butyl, hexyl, and octyl alcohols. In addition, weight loss determinations were done for n-heptane and n-hexadecane (cetane). Two PE bottle types were used in these studies, $\rho = 0.92$ g/cm^3 and $\rho = 0.940$ g/cm^3.

The ester and alcohol series showed a decreasing dependence of weight loss on increasing PE density at a given time. The low density bottle, $\rho = 0.920$ g/cm^3, showed a very large time dependence in weight loss while in the high density bottle, $\rho = 0.940$ g/cm^3, the time dependence was comparatively much smaller.

The weight loss for the ester series decreases from ethyl acetate to butyl acetate to amyl acetate with the first two members showing a slower decrease compared to the third member. The same relative weight loss behavior was observed in both density bottles and the loss rate for each member of the series appeared to be constant.

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[1] Laboratory for the Technology of Polymer and Rheology, CNR, Naples, Italy.

The weight loss for the alcohol series decreased from methyl to ethyl to propyl and increased to butyl to hexyl and subsequently decreased to octyl. The loss rates seemed constant for methyl through butyl, but appeared to show a large time dependence for hexyl and octyl. The same general behavior for each member of the series was observed for each density bottle, but the time dependence of the loss rate in the high density bottle appeared to have shifted to longer times compared to the low density bottle.

The weight loss and loss rate for the ester and alcohol series do not show a parallel behavior to that of the n-alkanes for the range of chain lengths investigated. The results do suggest that at large chain lengths there may be a better correspondence. These results further suggest that polarity and association effects for the early members of a homologous series greatly influence the relative behavior of the series to that of the n-alkanes and, therefore, compounds any quantitative correlations.

Optical Method of the Measurement of Transport Properties of Strained Polymer Samples

J. Phillips, A. Peterlin, and F. Waters[1]

An IR cell apparatus was designed and constructed for the purpose of determining transport and mechanical properties of transparent polymer films. The transport properties were measured from IR intensity changes of ethyl acetate vapor at the carbonyl frequency where the absorbance of the polymer was small or negligible. The mechanical properties of the film were determined simultaneously by using a load cell. The polymer, LDPE and PVF_2, were chosen to show the applicability of the IR cell to measuring conventional and nonconventional diffusion properties. The transport and mechanical properties of these polymers were extensively investigated in ethyl acetate vapor at $t = 30$ °C over a wide pressure and elongation range.

The results for PE/ethyl acetate showed that sorption and desorption were conventional and the diffusivity was approximately independent of the concentration of the vapor. The transport properties also showed a morphological transition at about $\varepsilon = 0.10$ for diffusivity and permeability while sorption increased continuously with strain to an apparent limiting value. The stress relaxation at vapor pressure, p, and cyclic sorption/desorption experiments showed an increasing difference between stress relaxation at $p = 0$ which indicated that structural changes were occurring as a function of time.

Polyvinylidene fluoride which has a $T_g \sim -38$ °C showed non-conventional or Type II behavior above a transition vapor pressure, p^*, and conventional behavior below p^*. On the imposition of a uniaxial tensile strain, transport properties and mechanical relaxation are enhanced and the transition pressure of ethyl acetate decreases. These results indicate that Type II behavior for PVF_2/ethyl acetate at a temperature above the glass transition temperature of the system depends on the pressure of ethyl acetate vapor as well as the strain level of PVF_2.

The IR technique is inherently limited to polymer/vapor systems in which the polymer has a high transparency in a region of the spectrum where the vapor has a strong absorption peak. In order for the absorbance to be correctly translated to actual concentrations, $c_v(t)$, corrections for changes in film thickness due to swelling and strain should be considered and properly applied.

Non-Linear Viscoelastic Behavior of Polymeric Materials

E. A. Kearsley, G. B. McKenna, and L. J. Zapas

The objective of this project is to capitalize on our considerable experience in characterizing non-linear viscoelastic behavior through constitutive equations. Methods of measuring strain-energy functions, time dependent strain-potentials and other determinants of mechanical behavior are developed. Methods of predicting specific material response to given tractions or deformations are developed. These results are of direct use in devising tests and standards for the mechanical suitability of materials for specific uses.

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[1] American University.

Part of this project is concerned with characterization of the extensional creep and stress relaxation behavior of carbon black filled rubber. We are using a modified form of the BKZ theory which accounts for the "damage" which occurs to the elastomer upon loading and unloading of the material in order to account for the accelerated creep and stress relaxation behavior observed in cyclic loading. This work will bear directly on the problem of failure of filled elastomers under fatigue loading conditions to the extent that we can describe the damage due to cycling using a constitutive equation and to the extent that a failure envelope describes the behavior of the filled elastomer. Experiments have been initiated to characterize the creep and stress relaxation behavior of the material and to obtain a failure envelope for the material. Cyclic creep, stress relaxation and failure behavior will also be characterized.

During the last year we substantiated a prediction made by the BKZ theory through experiments on both poly(methyl methacrylate) (PMMA) and a concentrated solution of poly (isobutylene) in cetane. The BKZ theory predicts that in a two step torsional stress relaxation history where the second step deformation, γ_2, is half of the first step deformation, γ, (i.e., $\gamma_2 = \frac{1}{2} \gamma_1$), then the second step normal stress response is predicted to be independent of the duration of the first step and equal to the response in a single step history at a deformation of $\gamma = \gamma_2$.

Also, during last year, we determined the time dependent strain potential derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_1$ for PMMA tubes. The results of this work indicate that $\partial W/\partial I_1$ is a negative at short times and becomes positive at high strains and long times. Such behavior is unusual and bears directly on the concept of using a shift in the mechanical relaxation spectrum to characterize the non-linear viscoelastic behavior of polymeric glasses. Work during the coming year will be undertaken using solid cylinders of PMMA rather than tubes to assure that the result is not an artifact of torsional measurements on a tube without applying an internal pressure.

Our recent work with the theory of rubber elasticity has shown that the strain-energy function for elastomers (which determines the non-linear elastic behavior) may be measurable from experiments simpler than hither-to thought possible. However, the method depends upon the strain-energy having a special form (the Valanis-Landel form). Although there is some data already in the literature which supports this requirement, there is also some published data which raises questions about its validity. The point needs clarification. We have devised a simple experimental test for the validity of the Valanis-Landel form which requires experiments of simultaneous extension and torsion of a cylinder. We will set-up equipment and conduct these tests for some typical elastomers this year.

In the coming year, the application of these methods to viscoelastic materials will also be pursued. It is hoped that these ideas will lead to a simplified method of obtaining extensional viscosity. Success in this venture will be of considerable significance since extensional viscosity is one of the most important parameters of polymer processing and it is ordinarily a very trying measurement.

Acoustic Emission of Crazing Polymers

A. Peterlin, R. Green, and J. Smith

Glass-bead epoxy resin composites and PMMA (commercial grade) were strained in an Instron Tensile Tester. Water and aceton induce crazing. Some acoustic emission was detected which was caused by the microcracking of the sample under the sharp dents of the grips. The Kaiser effect was also observed. The frequency spectrum of the acoustic emission by the growing crazes is probably so far below the response frequency of the sensor that the amplitude is not sufficiently above the background noise to be detected. Hence, only a small number of emissions could be registered. The method would permit a destructionless testing of the polymer specimen and of its load and deformation history if one can perform the experiment in a less noisy environment.

Elastic Modulus and Strength of Crystalline Polymers

A. Peterlin

The basic idea of the theory of both effects starts from morphological considerations. The existence of almost fully extended chains connecting the nearly rigid crystals through the much softer amorphous matrix is responsible for the high elastic modulus. The presence of the defects of the regular morphology causes the sample to fail. The situation is particularly simple in the fibrous structure when the axially oriented microfibrils with a great many tie molecules connecting the crystal blocks yield a high elastic modulus, up to 70 GPa in highly drawn linear polyethylene with E_c = 240 GPa (elastic modulus of the crystal in the chair direction). The defects of the microfibrillar structure are the ends of the microfibrils where the axial connection by taut tie molecules is drastically interrupted. Under the tensile load, the strain in such defects is many times higher than in the bulk sample, thus leading to microcrack nucleation and adjacent microfibril rupture. The effect is enhanced by a high elastic modulus to the microfibril. Consequently in a highly drawn sample the strain to break decreases with increasing draw ratio. In spite of the increase of the modulus the strength remains practically constant or increases much more slowly than the axial elastic modulus. The rupture of chains detectable by ESR is an effect which occurs during the straining of the sample although it does not determine the tensile strength.

Durability of Paper

J. C. Smith, E. E. Toth, and E. L. Graminski

The durability of paper is an important consideration in currency applications where replacement of worn out currency is a costly operation. The Bureau of Engraving and Printing supports work at NBS to characterize those aspects of the morphology of paper networks which affect durability with the objectives of improving durability and to achieve this improvement by replacing the presently used cotton and linen pulp with a less expensive pulp made from blended wood fibers.

Before these objectives can be realized, however, it is necessary to have an improved understanding of the relationship between the structure of paper, the morphology of the fibers, the processing conditions and the mechanical and physical properties of the paper and its components. Over the past several years studies on the bondability of pulp fibers at the National Bureau of Standards have helped to provide some of this background information.

Parameters for characterizing interfiber bond strength have been obtained from tensile tests on a low-density openweb handsheet prepared from the pulp to be evaluated. The force-elongation curve for a specimen from this handsheet contains numerous force drops, each drop caused by the breakage of a bond between fibers constituting the handsheet network. The relative number of bonds per unit area is characterized by the average elongation between bond breaks. The bond strength is characterized by an average of the force-drop magnitudes, by an average of the energy losses resulting from bond break, or by a characteristic elongation indicative of the stretch in the network needed to cause a break. These bonding parameters are being evaluated for handsheets of various areal densities, made from several different pulps that were subjected to various beating treatments. The morphologies of the handsheets and the constituent pulp fibers are being examined by optical and scanning electron microscopy.

Since the microstructure of the fiber network is influenced by the manner in which water is bound to the fibers, a part of this project is concerned with the characterization of water in pulps. Pulp fibers, especially chemical pulp fibers, are not suitable for paper manufacture as produced by a pulp mill. In order to make paper having suitable properties, it is necessary to subject the fibers to mechanical action. Mechanical action, such as beating or refining, causes fibers to imbibe water and to become more flexible. The more flexible a fiber becomes, the better it can conform with another fiber under pressure, which is the hallmark of interfiber bond formation. Fiber flexibility is also a factor in the formation of other physical properties essential to the paper conversion industry.

Part of the water imbibed by the pulp fibers is bound to the cellulose while the remaining water is considered to be free water. It is believed that the free water is most effective for fiber flexibility. As fibers are treated increasingly by mechanical action and imbibe more and more water, there is a question of whether the water sequentially imbibed is totally free water. There is the possibility that increased mechanical action can result in a decline in crystallinity and at some point the incremental imbibed water will be a combination of bound and free water.

The total water imbibed by a fiber can be measured by several methods, but the most frequently used method is by the solute exclusion principle. Weighted specimens of fiber and excess water are added to known quantities of solutions of high molecular weight material such as dextran, with a molecular weight of 2×10^6. The large dextran molecules cannot migrate into the cellulose fibers and thus the dilution of the dextran solution occurs by the water exterior of the fibers. The concentration of the dextran solution is measured accurately by polarimetry. The difference between the total water in the specimen and the amount of water which diluted the dextran is the water imbibed by the fibers. The water imbibed by the fibers is known as the fiber saturation point.

Water, bound to cellulose, does not freeze at temperatues down to 223 K, and this has been a means for measuring bound water. A method was developed for measuring bound water in pulps by means of differential scanning calorimetry. Weighed specimens of fiber and water were hermetically sealed then frozen. The amount of ice in each specimen was determined calorimetically and the total amount of water in each specimen was determined by drying the specimen to constant weight. The difference between the total water and the amount of ice in each specimen is equal to the amount of water bound to the cellulose.

Bound water and the fiber saturation point was determined for two beaten and unbeaten wood pulps and virgin cotton. The results indicate that beating has no effect on the crystallinity of wood pulps, but a significant effect on the crystallinity of cotton. Additionally, most of the imbibed water in beaten cotton pulp appears to be contained in the shortest fiber fraction. The longest fiber fraction in beaten cotton appears to imbibe considerably less water.

This large difference in the behavior of wood and cotton pulp during the mechanical action process apparently results in a significant difference in the microstructure of rag and wood pulp paper. This difference in microstructure may be the reason for the large difference in mechanical properties of cotton and wood pulp papers.

Configurations of Polymer Chains

R. J. Rubin

Configurations of Polymer Chains Interacting with Plane Interfaces--Treatment in Terms of a Random Flight or Diffusion Equation:

An isolated polymer chain in solution near a surface or between parallel surfaces will adopt various configurations depending upon the temperature and affinity of the links for the surface. A number of years ago, Rubin [1] and DiMarzio and Rubin [2] analyzed lattice models of the foregoing systems. In the absence of the complicating effects of interaction with surfaces, configurations of long chain molecules can be modeled by a random flight or diffusion equation. However, it is known from the lattice models that if the energy of attraction between links of the polymer chain and the surface are sufficiently high then there is a discontinuous collapse of the chain on the surface at a critical energy. The description of such discontinuous behavior within the framework of a diffusion equation appears to present technical difficulties. DeGennes [3] and Lépine and Caillé [4] have proposed a method of dealing with this problem in which the attractive (or repulsive) interactions of segments of the chain with a surface are treated in terms of a mixed boundary condition at the surface, i.e. $\ell \frac{\partial p}{\partial x} + mp = 0$ where p is the solution of the diffusion equation. I have investigated some of the ramifications of this approach and have calculated several quantities which appeared to be difficult to calculate within the framework of the lattice model:

1) the distribution function of the span of an adsorbed chain molecule at a plane solution surface in a direction normal to the surface, i.e., the distribution function of the thickness of the adsorbed molecule layer.

2) the distribution of the segments of a polymer chain confined between two parallel solution surfaces as a function of energy of interaction and chain length.

These calculations are in the process of being outlined in a paper for publication in the Journal of Chemical Physics.

Internal Configurations of Span Constrained Random Walks:

The spans of a random walk on a simple cubic lattice are the sides of the smallest rectangular box with sides parallel to the coordinate axes that entirely contains the random walk. The position of a random walker after N steps and constrained by a set of spans S_i is considered. In one dimension, if $S^2 \gg N$, the random walker tends to be located at the extremities of the span while in the contrary case the random walker is most likely to be found half-way between the extremities. In higher dimensions the position of the random walker in the direction of the largest span tends to lie at the span extremities while the position in the direction of the smallest span tends to be in the middle.

These calculations, performed in collaboration with G. H. Weiss of the National Institutes of Health, have been summarized in a paper which has been accepted for publication in the Journal of Statistical Physics.

Additional calculations are planned for other properties of span-constrained random walks including the statistics of occupancy within the rectangular box and the expected number of points visited.

1. R. J. Rubin, J. Chem. Phys. 43, 2392 (1965).

2. E. A. DiMarzio and R. J. Rubin, J. Chem. Phys 55, 4318 (1971).

3. P. G. deGennes, Rep. Prog. Phys. 32, 187 (1969).

4. Y. Lépine and A. Caillé, Can. J. Phys. 56, 403 (1978).

Polymeric Sealants for Geothermal Energy

E. A. Kearsley

The Department of Energy envisions that within a matter of decades the exploitation of geothermal energy resources will be making a substantial contribution to our national energy needs. However, in order for this to be accomplished, it is necessary to stimulate several associated technologies. The Division of Geothermal Energy of DoE has accordingly requested help in developing tests of polymeric materials to screen likely candidates for use as geothermal sealants. Since there are many forms of seals used in the drilling and production of geothermal wells and down-hole environments vary considerably among the different well locations, it is not possible to specify reasonable requirements for geothermal sealants in general. The most interesting and energetically important wells are potentially those with ambient down-hole temperatures greater than 260 °C and with strongly corrosive reducing (rather than oxidizing) atmospheres. The sealant materials should perform (frequently this means maintaining large elastic stresses for fixed deformations) under these demanding conditions for time periods ranging from hours for well-drilling sealants to months or years for production seals. Current technology for such seals is largely based on developments for the petroleum industry and is, consequently, adapted to lower temperatures and less corrosive, chemically different, conditions.

The program in the Polymer Science and Standards Division is currently beginning a survey of the needs and uses of sealants in the geothermal industry in order to understand the actual requirements for usage which a geothermal sealant material should meet. Concurrently, an experimental program is being designed to determine what features of the geothermal environment dominate the lifetime of sealants. Initially, materials will be aged at temperatures up to 260 °C (500 °F), probably in deformed states as well as in the natural state. Mechanical properties after aging will be measured. Eventually, concurrent aging of materials in conditions simulating a geothermal down-well situation (salts dissolved in water, 300 °C) will also be undertaken. A pressure cell suitable for this purpose is being set-up. Differences among materials aged in various atmospheres will be analyzed with the aim of isolating the important parameters of the aging atmosphere. The aim of this program is to contribute to the development of industry-accepted screening tests for geothermal polymer sealants.

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

J. M. Cassel

Task Leader

The objective of this research is to contribute to dental health care through development of better performing materials and test methodology and standards appropriate thereto. Materials research and techniques are pursued with the goal of developing adhesive composite restorative materials of greater durability and wear resistance, and improved base metal alloy alternatives to the costly gold alloy prostheses. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials and for defining the interactions that occur thereon.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense Medical R&D Command. Medical materials research is guided by close interaction with the National Heart, Lung, and Blood Institute and the ASTM F4 Committee (Medical and Surgical Materials and Devices).

Development of Adhesive Bonding Techniques

G. M. Brauer, R. L. Bowen[1], J. M. Antonucci, D. W. Misra[1]
J. S. Stansbury, E. E. Toth, and J. M. Cassel

A dentally applicable technique which established and maintained adhesive bonding would not only offer an important means for reducing the dental caries that is encouraged by percolation of fluids and bacteria at restoration margins but would afford a means of changing the mode of cavity preparation so as to reduce sound tooth structure destruction. Strong mechanical bonding of acrylic resins to enamel surfaces can be obtained through acid etching of such surfaces but such treatment is not applicable to the surfaces of dentin, the other major component of teeth. Such bonding has also not been entirely satisfactory in the caries-preventive application of pit and fissure sealants to the occlusal enamel surfaces of children's teeth.

A number of investigative routes to the development of adhesion to dentin are being followed. These include: synthesis of multi-functional methacrylate monomers that contain groups that can react with either the organic or inorganic portion of dentin; evaluation of cyanoacrylate-based systems; examination of urethane monomers that contain polymerizable methacrylates and residual isocyanates; synthesis and evaluation of multifunctional adhesion-promoting surface active amine accelerators; determination of techniques by which the polymerization shrinkage and resultant gap formation between restoration and cavity wall can be eliminated and investigation of tooth surface cleansing techniques and mordant treatments.

Initially, the bonding of cyanoacrylates to dentin or bone, a somewhat similar mineralized tissue, is very promising. However, the hydrolysis as the bonded specimens are aged or thermally cycled in water is extensive and debonding occurs rapidly. Attempts to slow down this deleterious effect of water have not been successful. Formulations containing various urethane-methacrylates and polymerizable diluents have developed initial bond strengths to dentin that are less than that attainable with cyanoacrylate and therefore are not satisfactory. Several surface-active amines when adsorbed to a powdered hydroxyapatite surface appear to be more reactive in the adsorbed state than when in solution and need further examination for their adhesion promoting ability. A number of isotonic, buffered acid solutions have been shown to remove the adhesion-inhibiting smeared layer produced at the surface of cut dentin and to do so without pulpal irritation. An isotonic ferric chloride mordanting solution has been found to form a modified dentin surface in less than 30 seconds and moderately improve adhesive bonding to composite resins.

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[1] American Dental Association Research Associate.

Dental Composite, Resin, Sealant, and Cement Chemistry and Development

G. M. Brauer, J. M. Antonucci, J. M. Cassel, R. L. Bowen[1],
H. Argentar[1], and D. W. Misra[1]

Early work in this laboratory resulted in a major breakthrough in the application of dental resin systems to restorative dental practice. Such materials constitute about one-fourth of all restorations placed per year. Because they are more durable than the silicate cements they replaced, considerable savings to the public is being accrued. However, deficiencies in the currently used commercial materials include: an ill-defined color stability problem; a high viscosity which requires dilution with lower viscosity compatible monomers for ease of application; insufficient storage stability except under ideal conditions; interfacial bonding of filler to resin that is inadequate for stress bearing applications; and a lack of capability for adhesive bonding to the tooth surface. Current efforts are directed toward providing solutions to these areas.

The approach to developing improved color stability involves synthesis and characterization of monomer systems: which are polymerizable at room temperature within the required time span for dental application; which employ minimal amounts of amine accelerators -- a source of color instability; which have a more hydrophobic character as a result of incorporating fluorine-containing monomers and should therefore be more stain resistant; which may use the eutectic mixture of crystalline methacrylate monomers as a means for eliminating color-prone impurities. Since some discoloration may originate in reactions with residual double bonds in the monomers, efforts are made to quantify such unsaturation. Such analysis is fairly straightforward in the resin matrix alone but difficult in the glass or quartz filler-reinforced composite. Infrared and Raman spectroscopy as well as differential scanning calorimetry are being applied to this problem. One route we are pursuing as a means of reducing residual unsaturation is to synthesize "prepolymer" monomers, e.g., oligomers or polymers which have reactive functional groups capable of generating further polymerization.

The influence of the type of viscosity-reducing methacrylate monomer diluents on the extent of marginal gap between composite restoration and cavity wall is being explored. Water sorbing diluents as well as those that can produce extensively cross-linked systems are being examined. A correlation is being sought between gap formation (and marginal leakage as determined with radioactive techniques) and properties of the monomer solution (e.g., viscosity, surface tension), and of the cured system (e.g., strength, indentation and recovery, and coefficient of thermal expansion).

To reduce tooth pulp toxicity response to the accelerator in dental composite restorations we are developing amine accelerators which generically should be less toxic and/or which are more efficient accelerators, and hence are required in lower concentrations for the polymerization. Two recently synthesized, very favorable amines for both toxicity and accelerating efficiency are N,N-dimethylaminophenethanol and N,N-dimethylaminophenylacetic acid. Efficiency of experimental amines is evaluated by measuring the speed of polymerization reactions as well as the minimal concentration of amine required to achieve polymerization at infinite time. A semi-automatic viscosity-measuring device to determine the state of polymerization has been designed and used in this work.

To determine specifically which components of a dental composite system, e.g., monomer, initiator, accelerator, inhibitor, U.V. absorber, etc., contribute most significantly to the tooth pulp response, collaborative projects have been initiated with the University of Florida and the Navy Medical Research Institute in Bethesda. A first phase result, based on pulp responses in primate teeth, did not indicate significant irritation with any one individual ingredient. Tests are now under way on combinations.

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[1] American Dental Association Research Associate.

Wear Resistance and Mechanical Properties

G. B. McKenna, J. E. McKinney, W. Wu, and J. M. Cassel

An immediate objective of this effort is to demonstrate that data can be obtained with an accelerated laboratory test that will predict the durability of composite restorative materials when they are used in stress bearing situations. Such a test procedure would eliminate the need for very costly clinical trials that are now required. A second principal objective is to define the mechanism of the wear process that occurs clinically and to determine the physical test procedures and the data that will enable a correlation to be made between the physical-mechanical properties of the composite system and its durability. This correlation will serve to expedite development of more durable, stress resistant composite systems.

The third version of the wear apparatus was essentially completed during FY79. The new version determines the wear track length by counting revolutions rather than determining the product of an assumed angular velocity and time interval. By using "depth" measurements on flat brass discs that are not contacted by a wear pin, we have determined that in over 40,000 revolutions the experimental uncertainty itself will not exceed 0.5 μm. Measurements made at ten positions around a circular wear track in both amalgam and composites indicate there are inhomogeneous regions in specimens as we have prepared them. One factor which appears may influence the results with amalgam is the force applied in condensing the amalgam disc specimens. Results to date indicate we may be able to employ synthetic durapatite pins as substitutes for those we derived by careful and tedious grinding of human tooth enamel.

An effort has been initiated to determine the relationship, if any, between wear resistance and the fatigue behavior of composite systems. The approach utilizes the concept of damage accumulation that has been elucidated by others working the Polymer Science and Standards Division on mechanical properties of polymers. By cycling materials to various fractions of their lifetime and then conducting wear measurements on the fatigued samples, the effect of the state of damage on wear rate is explored.

A second approach being taken to correlate the mechanical properties of dental composites with wear behavior is the study of the resistance of these materials to crack propagation. The study of fracture toughness and fatigue crack propagation along with the fatigue/wear investigations should enable us to determine the contribution of these parameters to the wear of dental composites.

Because the BIS-GMA system commonly used in commercial dental composites is extremely brittle, a factor which should work to reduce their wear resistance, we have initiated efforts to develop methods for toughening the system by incorporating elastomeric components.

Dental Alloy Ceramic and Implant Research

J. A. Tesk, R. P. Whitlock[2], E. E. Parry[2], C. P. Mabie[1],
R. M. Waterstrat[1], and D. L. Menis[1]

Despite the difficulties encountered in handling dental gold alloy alternatives, 25% of all porcelain veneered crowns are now constructed of Ni-based alloys. This investigation is designed to determine the characteristics of base metal casting alloys and associated bonding porcelains in relation to the feasibility of their use in cast crowns and fixed partial dentures; to determine the effects of fabrication techniques on the clinical serviceability of the restorations; to explore the overall problem of bonding dental ceramic materials to metal substrates; and to fabricating these porcelain/metal restorations.

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[1] American Dental Association Research Associate.
[2] U.S. Navy Research Associate.

The goal is also to determine new or improved methods and techniques for fabrication of prostheses from dental alloys and veneering materials; development of new alloys and veneering materials in consideration of those needs and the need for reliable sources of raw materials; investigate new approaches for manufacture of dental porcelain and the incorporation of fluorescing agents into porcelain; examine opportunities for modification of operative techniques involving subperiosteal implants through changes in materials and material properties employed and conduct feasibility study for stress analysis-aided improvement in implant design; and implement experimental studies for improvement of mechanical properties and material handling characteristics of methacrylate resin based bone cement with possible applications for dental implant, as well as orthopedic procedures.

Porcelain Fused to Base Metal Alloys

R. P. Whitlock[1], J. A. Tesk, and E. E. Parry[1]

The characterization of ceramic materials available for bonding to dental casting alloys has progressed quite well. The measurement of dimensional change resulting from thermal cycling has been completed for nearly all ceramic specimens. The degree of expansion/contraction of the ceramic materials relative to the same properties in the substrate alloys during recommended firing schedules must be compatible in order to minimize the build-up of excessive stress in the materials which could result in brittle fracture of the porcelain in the completed restoration. Interfacial stress can be increased markedly through a "mismatch" of these properties. The data collected thus far indentify considerable variation in the expansion/contraction characteristics among different manufacturers' ceramic products. Further, these changes appear to be linked directly to the thermal history of the specimen, i.e., the number of firing cycles to which the material is exposed during fabrication processes. Generally, it would appear on early examination of the data that the expansion coefficient (α) increases with repeated thermal cycling. However, this phenomenon does not manifest the same way for all materials. Further observations suggest that qualitative and/or quantitative changes in crystallinity of the ceramic materials may develop as a function of thermal history. Early results from x-ray diffraction analyses indicate that, indeed, crystal patterns are different in these specimens. Further study in this area is under way at this time to ascertain the extent of crystalline conversion that is occurring and to correlate these differences with changes in the refractory nature of the materials. These observations may have major operational significance inasmuch as some ceramic materials, apparently, can withstand more (repeated) exposure to high temperatures during laboratory fabrication processes without showing appreciable changes in either α or phase structure.

The ability of ceramic powders to "wet" substructure alloy surfaces during the fusion process is a critical element in promoting chemical and mechanical interaction at the interface which is necessary for accomplishing optimum bonding of the materials. Analyses of particle size distributions among the various porcelain manufacturers' products have been completed and the data are being examined. Some differences in this regard have been found to exist among the products examined. Specific combinations of alloys and bonding porcelains have been fused together and are presently being analyzed via void (no contact) formation at the interface for completeness of "wetting." Variations in alloy surface preparation, preconditioning of the substrate (oxidation) and (opaque) porcelain application techniques are being evaluated to ascertain the effects of these variables on the wetting process. Preliminary analysis of the data collected in this phase of the investigation would suggest that 1) variations in porcelain alloy combinations influence the area of contact between the materials after fusion, and 2) different techniques used for applying (opaque) porcelain powders to the alloy substrate may alter the completeness of the "wetting" process. Knowledge gained from the foregoing experiments should assist greatly in more appropriate selection or matching of compatible alloy/porcelain combinations as well as fabrication techniques.

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[1] U.S. Navy Research Associate.

Corrosion, Base Metal Alloys

J. A. Tesk

The extent to which pitting corrosion might be predicted in a clinical situation for a given alloy of a given composition and microstructure is of importance for at least two reasons: 1) the greater the degree of pit formation, the more the tendency for plaque formation with its accompanying undesired organic acid release, and 2) the pit formation process must of itself release ions to the surrounding medium that may be deleterious in one way or another. Availability at NBS of extensive expertise and instrumentation in the area of corrosion and alloy microstructure determination and the presence on the staff of a guest worker from the University of Düsseldorf for a year with a strong interest in this area allowed an immediate attack on this phase of our base metal alloy effort.

Three Ni-Cr alloys representing typical materials of this kind have been investigated. These materials not only consist of different chemical compositions but their microstructures which were observed by light micrographs and SEM exhibit major differences. One appears to be almost single phase with only a few precipitates within the grain whereas the other two show a eutectic constituent in the microstructure. Anodic polarization curves of as cast and fire-cycled samples were generated and breakdown potentials determined in artificial saliva solution adjusted to pH 3.2. This preliminary work points toward a lower in vitro corrosion resistance in a Be-containing alloy with a eutectic constituent in its microstructure.

New Dental Ceramic Directions

C. P. Mabie[1] and D. L. Menis[1]

Porcelain frits have been developed which fuse at lower temperatures than current commercially available porcelains. These were prepared by the calcination of gelatinous precipitates and have fusion temperatures in the range 900 to 930 °C. Thermal expansion coefficients of these porcelains, which determine matching of the porcelain to gold alloy or base-metal substrates, are near those of commercial porcelains fusing at higher temperatures.

To strengthen porcelains, quartz and alumina grains and glass fibers are being dispersed into the gels. Attempts are being made to fabricate micacaeous porcelains that are stronger and more machinable. Emphasis is being placed, also, on development of porcelains with small working-range temperatures so that interfacial stresses, which often result in porcelain-to-metal bond failures, can be relaxed.

Investigation of new investments for the casting of base-metal alloys continues. The objectives are to develop investments that are less susceptible to mold reactions and in which most of the dimensional compensation can be obtained thermally. Zirconium phosphate and aluminum phosphate bonded investments, with flint refractory grains, are to be studied. Investments more suitable for making routine dental castings from titanium alloys are being investigated.

Irradiation Effects from Neutron Activated Dental Materials

J. A. Tesk

As a result of the very limited information available in the literature, calculations have been made to estimate the effects of secondary radiation from gold crowns receiving neutron irradiation. Gold is the only element examined to date and was chosen because of its high neutron activation cross section, relatively short half life (2.7 days), and its extensive use as a dental restorative material. Estimates on γ and β radiation doses delivered to soft tissue were made for single crowns and a mouth full of crowns. A 50 REM neutron exposure was assumed as this is clearly a sublethal exposure. The results are that a single gold crown is likely to provide an additional 2 REM γ dose to local tissue and six or more adjacent crowns provide an additional dose between 3 and 5 REM. It is estimated that the local tissue can receive a β dose of at least 25 REM following a 50 REM neutron dose.

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[1] American Dental Association Research Associate.

It has been calculated that temporary shielding of local tissues from maximum energy β radiation from gold is possible by using 0.40 cm of ordinary mouth guard material. The use of higher density materials decreases the thickness of shielding required according to the relationship $t\rho = 0.40$, where t is the thickness and ρ the density. However, for subgingival restorations, shielding is virtually impossible.

Dental Implants

J. A. Tesk

No viable dental implant exists except for what has become known as the subperiosteal implant. This implant, while particularly well suited for older edentulous patients who have suffered severe loss of bone to the extent that the use of conventional dentures is ineffective, might find greater usage if the lengthy operative procedures could be reduced. Simplification of the procedure via development of a heat treatable, biocompatible alloy system which could be formed to fit the bone while in the dead soft condition is being considered. The time required to wax, invest, cast, clean, polish, and transport the implant might be eliminated and the total time for a one-day procedure reduced from 12-13 hours to 3-5 hours.

Much of the current interest in dental implants centers around theoretical analysis to provide a more clear understanding of the effects of stress on bone with anticipation that implants may be more effectively designed by individuals armed with such knowledge. Much fundamental information of these stress effects is not yet available. Efforts to collaborate with the University of Illinois in developing extended studies of stress in oral tissue using finite element techniques are being finalized.

Clinical and Laboratory Investigation of Dental Amalgams

N. W. Rupp[1], G. C. Paffenbarger[1], and R. M. Waterstrat[1]

Amalgam restorations account for 70% of all restorations currently placed. The reasons for their progressive deterioration are not as well understood as is desired. Seven-year-old amalgam restorations are being observed for margin integrity, tarnish, corrosion, and change in contour. These clinical observations corroborate laboratory results which show that amalgams having high creep values tend to "grow" or extrude out of the cavity. This growth is not necessarily caused by repeated loading of the tooth but, as observed earlier, the amalgam expands as a result of continuous changes in phases within the amalgam. As these phase changes take place, forces are generated which cause expansion; however, amalgams having low creep values are restrained in their dimensional changes by the cavity walls.

Recently it has been observed that alloys which do not contain zinc have very little expansion even when unrestricted as compared to those which contain zinc. This raises questions concerning the role of zinc in these silver alloys. Specifically, does zinc facilitate phase changes? If so, can zinc be removed from all alloys, thus reducing the phase changes and, consequently, the forces which might result in unwanted expansion of the amalgam restorations?

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[1] American Dental Association Research Associate.

Also, we observed that the creep values of certain amalgams are increased by an increase in mercury content; other amalgams were not as sensitive to this increase in mercury content. Nonetheless, amalgams should be mixed and inserted so that the restoration will have the lowest possible mercury content. Even the recently-introduced alloys that use approximately 45% mercury in the original mix should have only 39-41% remaining in the restoration.

It now appears that the elimination of the weak and corrosion-prone tin-mercury phase does not always produce a more durable amalgam, and claims for such an effect have apparently been exaggerated. Some other factors must be partly responsible for the demonstrated clinical superiority of the copper-containing amalgams. Resistance to creep and corrosion are certainly desirable characteristics, but it is not clear how these can best be achieved. Recent experiments showed that small amounts of manganese dissolved in the conventional silver-tin alloys produce amalgams with a sharply reduced creep and that the maximum reduction in creep may be achieved without sacrificing essential corrosion resistance. This is accomplished by optimizing the ratio of the copper and manganese contents so that the manganese content is minimized. The manganese not only tends to eliminate the tin-mercury phase, but it also seems to inhibit the formation of other phases. We are hopeful that this will help to prevent gradual breakdown of the margins and occlusal surfaces and prolong the useful life of the restoration.

Dental Enamel Chemistry and Preventive Dental Treatments

W. E. Brown[1], L. C. Chow[1], M. Mathew[1], and G. L. Vogel[1]

The objective of this project is to develop and apply fundamental information on the solubility and crystallographic structure of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with 1) development of physicochemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated into tooth enamel, and 2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid etch bonding treatments and improved topical fluoride procedures.

Crystallographic research is utilized to provide a sound structural basis for understanding the chemical properties of the calcium phosphates in tooth, bone, dental calculus, and those that are formed or used in dental therapy. The chemical reactivities of calcium phosphates are structure dependent; this program continues to be the major source of structural information on these compounds for the National Institute of Dental Research. Recently a new project was commenced that is capable of providing powerful insight into the mechanism of growth of tooth and bone crystallites. This mechanism, which involves interlayering of enamel mineral with another calcium phosphate, was shown to be valid for crystals grown _in vitro_. If this proves valid for enamel mineral _in vivo_, it will be a major step forward in understanding both the role of fluoride in preventing caries and the mechanism that causes enamel mineral to incorporate impurities, e.g., carbonate, that affect its resistance to caries. An ultra-micro technique is being used to study the effects of demineralizing environments on the composition of solutions within incipient carious lesions in human enamel. The objective is to gain an increased understanding of the events that control lesion formation. This _in vitro_ study has produced, for the first time, information on pH changes within enamel and membrane potentials across the enamel surface when the specimen is undergoing demineralizing processes.

The effectiveness of an experimental topical fluoridation procedure has been examined in an animal study in collaboration with the National Institute of Dental Research. The procedure consists of a pretreatment with a calcium phosphate solution capable of forming the crystalline compound $CaHPO_4 \cdot 2H_2O$ in the enamel. This is followed by a fluoride treatment to convert the newly-formed salt into an insoluble form of tooth enamel. The new procedure resulted in significantly higher fluoride uptakes compared to conventional sodium fluoride or stannous fluoride treatments. Animals that received the new treatment procedure also had the lowest mean caries scores, but this result was not highly significant from a statistical point of view. Further studies of the new procedure were carried out in cooperation with the School of Dentistry, Taiwan University. A single application of the commercial topical acidulated phosphate fluoride solution (APF), preceded by a treatment with the $CaHPO_4 \cdot 2H_2O$-forming solution, yielded a mean fluoride uptake of approximately 2000 ppm when measured three months after treatment. The mean fluoride uptake from a single APF treatment control experiment was only 100 ppm and was not statistically significant. It appears that, under clinical conditions, the new topical fluoridation procedure produces fluoride uptakes that are much greater than have been obtained by fluoride agents presently in use. This procedure could prove to be a major step forward in fluoride therapy.

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[1] American Dental Association Research Associate.

Phosphoric acid etchants are now in frequent use for pit and fissure sealants, cementing of orthodontic brackets, and repair of incisal edges. It previously had been shown that partial saturation of the etching solution with calcium and phosphate would reduce the loss of mineral in the initial stage of etching. It remained to be shown, however, that the new etching procedure would produce enamel surfaces to which plastic would adhere. Laboratory tests have now shown that the new solutions were at least as good as the ones in use and do not cause potentially harmful loss of enamel. The new procedure warrants clinical evaluation.

Dental and Medical Materials Standards

J. M. Cassel, G. M. Brauer, J. A. Tesk, and N. W. Rupp[1]

Active participation from Task Force level to the role of Subcommittee Chairman, occurs in development of dental standards through ANSI MD 156 and ISO TC 106, Dental Materials and Services. Development of medical implant standards is assisted by serving in roles of Polymeric Materials Chairman and Task Force leadership in the efforts of ASTM F4, Medical and Surgical Materials and Devices, and as Chairman, USA TAG ISO TC 150, Surgical Implants.

Molecular Weight Dependence of Polymer Adsorption on Solid Surfaces

W. H. Grant and R. E. Dehl

The adsorption of polymer molecules on solid surfaces is being investigated for both theoretical and practical reasons. The nature of the interaction of large molecules with surfaces is relevant to the problem of adhesion faced in medical cardiovascular implant application, dental plaque accumulation, and in securing plastic coatings to surfaces in a multitude of end uses. This interaction also has an important role in the strength and stability of polymer composite materials. It is fundamentally important to understand the changes which occur in the conformation of a long-chain molecule when it interacts with a surface. The number of points of attachments at the surface and the distribution of adsorbed segments, loops, and tails are all relevant to the stability and integrity of the polymer-substrate interface.

Previous work at NBS and elsewhere has provided significant insight into the understanding of this problem. However, recent theoretical and experimental studies by a group from the Agricultural University in The Netherlands is casting doubt on some of the accepted precepts about polymer adsorption. For example, it has been commonly believed that the adsorption of macromolecules is an irreversible process. According to the recently developed theory, however, polymer molecules are not necessarily adsorbed irreversibly, but desorption always occurs by the displacement of short chains by longer ones in the supernatant solution. Phenomena such as the rounded shape of the adsorption isotherm, the dependency of the adsorbance on the solution concentration, and the absence of desorption upon dilution are explained in the current theory by polydispersity of the polymer.

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[1] American Dental Association Research Associate.

The predictions of the displacement theory are currently being tested by the use of radiolabeled polystyrene fractions having narrow molecular weight distributions. To date, studies have involved only one radiolabeled component in a binary mixture, which has left ambiguities in the interpretation of results. Future studies will involve the use of two different radiolabeled species, with a different nuclear tag on each species. In this way, the adsorption and displacement behavior of the different molecular weight species will be examined in detail.

Invited Talks

"Synthesis of Polyfluorinated Polymethacrylates for Dental Applications"
IADR & AADR 57th General Session and Annual Session,
New Orleans, Louisiana
J. M. Antonucci
March 1979

"Composite Restorative Materials"
15th Annual Meeting Brazilian Dental Materials Group,
Florianopolis, Brazil
Dr. R. L. Bowen
July 1979

"Effect of Diluent on the Properties of BIS-GMA Based Composites"
(IADR & AADR)
57th General Session and Annual Session,
New Orleans, Louisiana
G. M. Brauer
March 1979

"New Amine Accelerators for Dental Composites"
ACS Meeting
G. M. Brauer
September 1978

"Two Types of Pyroelectricity in a Copolymer at Vinylidene Fluoride & Tetrafluoroethylene"
International Workshop on Electric Charges in Dielectrics,
Kyoto, Japan
M. G. Broadhurst
October 1978

"Piezoelectric Polymer Transducers"
NBS Conference Room - Science and Technology Attaches visit
M. G. Broadhurst
May 1979

"Piezoelectric Polymers"
18th Annual Meeting of the Plastics Institute of America
United English Center, New York, New York
M. G. Broadhurst
April 1979

"Piezoelectricity & Pyroelectricity in PVDF - A Model"
(CEIDP) Pocono, Pennsylvania
M. G. Broadhurst & G. T. Davis
October 1978

"Basis of Piezoelectricity in PVDF"
Univ. of Tokyo (Japan)
M. G. Broadhurst
October, 1978

"Polyvinylidene Fluoride Viewed as a Polycrystalline Ferroelectric Material"
Kyoto, Japan
M. G. Broadhurst
October 1978

"Electrical Properties of Polymers"
Waseda University, Japan
M. G. Broadhurst
October 1978

"Basis of Piezoelectricity in PVDF"
Kyoto University, Japan
M. G. Broadhurst
October 1978

"Current Developments in Piezoelectric Polymer Research and Applications"
Bell Labs, Murray Hill, New Jersey
M. G. Broadhurst
August 1979

"Piezo- & Pyroelectricity in Polymers" Part of 1979 Summer Institute in Polymer Science and Technology, University of New York, New Paltz, New York
M. G. Broadhurst
June 1979

"Cooperative Molecular Rotations in a Ferroelectric Polymer"
NBS Colloquim on Mathematical Modeling in Science and Engineering,
NBS
M. G. Broadhurst
August 1979

"NBS Pyroelectric and Piezoelectric Polymer R & D: I. Structure Activity and Use"
National Bureau of Standards, Washington, D. C.
M. G. Broadhurst
January 1979

"Some Aspects of Poling PVDF"
Army Research Office Workshop on Piezoelectricity,
Dover, New Jersey
M. G. Broadhurst
January 1979

"Piezoelectric Polymers"
Video taped for future file on WDVM-TV, Steve Gendel, interviewer
M. G. Broadhurst
July 1979

"Kinetics of Hydrolytic Aging of Polyester Polyurethane Elastomers"
ACS National Meeting, Washington, D. C.
D. W. Brown
September 1979

"Mechanisms of Action of Fluoride in Prevention of Dental Caries"
ACS/Japan Chemical Congress, Honolulu, Hawaii
W. E. Brown
April 1979

"A Testing Program for Porous Polymer Tapes"
EPRI - Seminar on Solid Dielectric Materials,
Monterey, California
A. J. Bur
January 1979

"Lifetime Behavior of Polyethylene Bars in Uniaxial Extension
in Various Chemical Environments"
American Chemical Society, Miami, Florida
J. M. Crissman
September 1978

"Lifetime Behavior of Polyethylene Sheets Under Inflation in the
Presence of Stress-Cracking Agent"
American Chemical Society, Washington, D. C.
J. M. Crissman
September 1979

"Static Fatigue of Polyethylene in Uniaxial Creep in the Presence
of Stress-Cracking Agents and Solvent"
American Chemical Society, Washington, D. C.
J. M. Crissman
September 1978

"Progress Report on Mechanical Properties Studies Relevant to the
Performance of Plastic Packaging for Hazardous Materials Transportation"
Public Meeting on Polyethylene Packagings held at the Department
of Transportation, Washington, D. C.
J. M. Crissman
July 1979

"Piezo- & Pyroelectric Polymers - Mechanisms & Application"
Gordon Research Conference, Program on Polymers,
New London, New Hampshire
G. T. Davis
July 1979

"Poling of PVDF at High Electric Fields"
CEIDP - Pocono, Pennsylvania
G. T. Davis
October 1978

"Charging of Polymer by High Electric Fields"
Conference on Electrical Insulation and Dielectric Phenomenon,
Pocono, Pennsylvania (CEIDP)
A. S. DeReggi, M. G. Broadhurst
October 1978

"Research in the Polymer Science and Standards Division"
Solar Energy Research Institute, Golden, Colorado
R. K. Eby, L. E. Smith and B. M. Fanconi
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
Washington State University, Pullman, Washington
R. K. Eby
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
University of Washington, Seattle, Washington
R. K. Eby
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
University of Tennessee, Knoxville, Tennessee
R. K. Eby
February 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Proctor and Gamble Corporate Central Research Laboratories,
Cincinnati, Ohio
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
March 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
General Motors Research Laboratory, Warren, Michigan
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
June 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Boeing Research Laboratory, Renton, Washington
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
June 1979

"Dynamic Measurement of Nip Pressures"
10th Annual Symposium on Paper Properties & Technology,
Oxford, Ohio
S. Edelman
May 1979

"The Adsorption of Human Serum Albumin and Gamma Globulin on Hydrophobic and Hydrophilic Surfaces"
Joint Meeting of the Japanese Chemical Society and the American
Chemical Society,
Honolulu, Hawaii
Warren Grant
April 1979

"Temperature & Molecular Weight Dependence of Polymer Dimensions in Solution"
IBM Laboratories, San Jose, California
C. C. Han
January 1979

"Some Nonlinear Effects in Polymer Testing"
Subcommittee on Geothermal Seals of ASTM, Committee D11.36,
Minneapolis, Minnesota
E. A. Kearsley
June 1979

"Dental Investments"
Wilford Hall USAF Medical Center, Lockland AFB,
San Antonio, Texas
C. P. Mabie

"The Crystal Structure of $Pb_8K_2(PO_4)_6$: An Apatite Without Hexed Anions"
American Crystallographic Assoc. Meeting, Honolulu, Hawaii
Dr. Mathai Mathew
March 1979

"Measurement of Molecular Weight Distribution by Recycle Size Exclusion Chromatography"
ACS National Meeting, Washington, D. C.
F. L. McCrackin
September 1979

"Time Dependent Failure Behavior of Glassy and Semi-Crystalline Polymers"
IBM, San Jose Research Laboratories, San Jose, California
G. B. McKenna
January 1979

"Time Dependent Failure of PMMA and Polyethylene"
Naval Research Laboratories, Chemistry Division Seminar,
Washington, D. C.
G. B. McKenna
February 1979

"Development of Fiber Reinforced Polymer Composites for Orthopedic Applications"
3M Corporate Research Center, St. Paul, Minnesota
G. B. McKenna
June 1979

"Time Dependent Processes in Polymeric Materials - Viscoelasticity and Failure"
University of Minnesota, Department of Chemical Engineering,
Minneapolis, Minnesota
G. B. McKenna
June 1979

"Low Temperature Dielectric Loss Characterization of Polypropolene"
(CEIDP) Pocono, Pennsylvania
F. I. Mopsik
November 1978

"Physical Testing of Polymers for Use in Circulatory Assist Devices"
Second Annual Contractors Meeting, Devices and Technology Branch,
NIH, Bethesda, Maryland
R. W. Penn
December 1978

"A Defect Which Transports a Polymer Chain Along the Molecular Axis"
Universität für Makromolekulare Chemie der Albert Ludwigs
Universität, Freiburg, West Germany
D. H. Reneker
September 1978

"A Defect Which Transports a Polymer Chain Along the Molecular Axis"
Universität Ulm, Ulm, West Germany
D. H. Reneker
September 1978

"Diffusion in Polymers"
Josef Stefan Institute, Ljubljana, Yugoslavia
D. H. Reneker
October 1978

"Localized Defects in Polyethylene and the Use of Infrared Absorption to Measure the Number of Trans-gauche Bond Pairs"
Instituto di Chimica del Politecnio, Milano, Italy
D. H. Reneker
October 1978

"Nuclear Magnetic Resonance Line Shape, Relaxation and Self-Diffusion of Polyethylene in the Melt"
American Physical Society Meeting, Chicago, Illinois
D. H. Reneker
March 1979

"Overview of Technical Activities of the Polymer Science and
Standards Division of the National Bureau of Standards"
Picatinny Arsenal, Army Armament R & D Command, Dover, New Jersey
D. H. Reneker, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
May 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Lawrence Livermore Laboratory, Livermore, California
D. H. Reneker, M. G. Broadhurst, and B. M. Fanconi
July 1979

"Transport of a Polymer Chain in a Crystal Lattice in the Axial Direction"
IUPAC 26th International Symposium on Macromolecules, Mainz,
West Germany
D. H. Reneker
September 1979

"Detecting and Monitoring Deterioration in Bearings Using Piezoelectric Polymer"
Symposium on Detection Diagnosis & Prognosis System Applications,
San Antonio, Texas
S. Roth
November 1978

Discussant at Winter Gordon Conference on Polymers
Santa Barbara, California
R. J. Rubin
January 1979

"Enzyme-enzyme Interactions, Diffusion, and Steady-State Kinetics"
American Physical Society Meeting, Chicago, IL
R. J. Rubin
March 1979

"Effect of Enzyme-Enzyme Interactions on Steady-State Enzyme
Kinetics: Some Exact Results in a Lattice-Fluid Model"
International Symposium on Mathematical Topics in Biology,
Kyoto, Japan
R. J. Rubin
September 1978

"Effect of Enzyme-Enzyme Interactions on Steady-State Enzyme
Kinetics: Some Exact Results in a Lattice-Fluid Model"
Seminar, Physics Department, Waseda University, Tokyo, Japan
R. J. Rubin
September 1978

"Selection and Use of Dental Materials"
U. S. Air Force, Andrews AFB, Maryland
Dr. N. W. Rupp
May 1979

"Dental Materials - Their Selection - 1979"
College of Dentistry, Ohio State University, Columbus, Ohio
Dr. N. W. Rupp
June 1979

"Statistical Thermodynamics of Polymer & Oligomeric Mixtures"
Gordon Research Conference on Polymers, Santa Barbara, California
I. C. Sanchez
January 1979

"Statistical Thermodynamics of Polymer Solutions"
E. I. duPont de Nemours, Wilmington, Delaware
I. C. Sanchez
May 1979

"Statistical Thermodynamics of Bulk and Surface Properties of Polymer Mixtures"
Joint US/Japan Conference on Multi-component Polymers,
Kyoto University, Japan
I. C. Sanchez
December 1978

"High Resolution Solid State ^{13}C NMR in Polymers"
Chemistry Department Seminar, University of Maryland,
College Park, Maryland
D. L. VanderHart
November 1978

"High Resolution ^{13}C NMR of Solid Polymers"
Chemical Society of Washington, Topical Session, NIH,
Bethesda, Maryland
D. L. VanderHart
February 1979

"Spin-Spin and Spin-Lattice Contributions to ^{13}C Rotating Frame Relaxation and Linewidths in Polymers"
Gordon Research Conference on Magnetic Resonance,
Wolfsboro, New Hampshire
D. L. VanderHart, William L. Earl, & A. N. Garroway

"Expectations for Resolution in High Resolution ^{13}C NMR of Solids: Particularly Polymers"
21st Annual Rocky Mountain Conference on Analytical Chemistry,
Denver, Colorado
D. L. VanderHart
July 1979

"^{13}C NMR Studies of Semicrystalline Polymers: Polyethylene and Cellulose"
Sixth Annual Meeting of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Pennsylvania
D. L. VanderHart
September 1979

"Stress-Strain-Time Diagrams, Including Failure Envelopes for High Density Polyethylenes of Different Molecular Weight"
American Chemical Society, Miami, Florida
L. J. Zapas and J. M. Crissman
September 1978

"Small Deformations Superimposed on Large Deformations for Non-Linear Viscoelastic Materials"
Department of Mechanical Engineering,
University of Maryland, College Park, Maryland
L. J. Zapas
April 1979

Publications and Patents

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A. Ziya Akcasu and Charles C. Han
Macromolecules, 12, 276-280 (1979)

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L. Araimo, F. deCandia, V. Vittoria, and A. Peterlin
J. Poly. Sci. (Phys. Edition), 16, 2087-2103 (1978)

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J. D. Barnes, G. M. Martin, and F. L. McCrackin
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"Critical Review of Vibrational Data & Force Field Constants for Polyethylene"
John Barnes and Bruno Fanconi
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"The Influence of Polymer Membrane Properties on the Performance of Dissolved Oxygen Sensors"
John D. Barnes
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"SRM 1470: Polyester Film for Oxygen Gas Transmission Measurements"
John D. Barnes and Gordon M. Martin
NBS Special Publication, 260-58 (1979)

"Adhesive Bonding of Various Materials to Hard Tooth Tissues XVIII: Synthesis of a Polyfunctional Surface-active Comonomer"
R. L. Bowen
J. Dent. Res. 58(3): 1101-1107 (Mar. 1979)

"Adhesive Bonding of Various Materials to Hard Tooth Tissues--Solubility of Dentinal Smear Layer in Dilute Acid Buffers"
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International Dental Journal, 28(2): 97-107 (1978)

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G. W. Bradley, G. B. McKenna, H. K. Dunn, A. U. Daniels, and W. O. Stratton
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G. M. Brauer
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"Properties of Sealants Containing Bis-GMA and Various Diluents"
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J. Dent. Res. 57(4): 597-607 (April 1978)

"Formation of a New Crystal Form (α_p) of PVDF Under Electric Field"
D. Naegele, D. Y. Yoon, and M. G. Broadhurst
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"On the Calculation of Piezoelectricity and Pyroelectricity in Polyvinylidene Fluoride"
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"The Radiation-Induced Copolymerization of Tetrafluoroethylene & Styrene at High Pressure"
Daniel W. Brown and Robert E. Lowry
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Daniel W. Brown and Robert E. Lowry
J. Poly. Sci., Polymer Chemistry Edition, 17, 1039-1046 (1979)

"Crystallinity in Hydrolytically Aged Polyester Polyurethane Elastomers"
Daniel W. Brown, Robert E. Lowry, and Leslie E. Smith
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"Interlayering of Crystalline Octacalcium Phosphate and Hydroxylapatite"
W. E. Brown, L. W. Schroeder, and J. S. Ferris
J. Phys. Chem., 83, 1385 (1979)

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W. E. Brown
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"Pyrolysis Gas Chromatography of Some Fluorine-Containing Polymers"
Constantin N. Cascaval and Roland E. Florin
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"Lifetime Behavior of Polyethylene Bars in Uniaxial Extension in Various Chemical Environments"
J. M. Crissman
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"Stress Strain-Time Diagrams, Including Failure Envelopes, for High Density Polyethylenes of Different Molecular Weight"
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"Creep Failure and Fracture of Polyethylene in Uniaxial Extension"
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"Lifetime Behavior of Polyethylene Sheets Under Inflation in the Presence of Stress-Cracking Agent"
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"Experiences in Developing an Automated Factor-Jump Method of Thermogravimetry"
Brian Dickens
Thermochimica Acta, 29, 87-113 (1979)

"Computer Program to Implement Automated Factor-Jump Thermogravimetry"
Brian Dickens
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"Automation of Factor-Jump Thermogravimetry for Active Computer Control"
Brian Dickens
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"Evaluation of Commercial and Newly-synthesized Amine Accelerators for Dental Composites"
Dianne M. Dulik
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"Observations in Solid Polyethylene by ^{13}C NMR with Magic Angle Sample Spinning"
William L. Earl and D. L. VanderHart
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"Energetics of Methyl Branches in Hydrocarbon Crystals"
B. L. Farmer and R. K. Eby
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"Free Radicals in Stretched Vinylidene Chloride Copolymer"
Roland E. Florin
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"Application of New Kinetic Techniques to the Lifetime Prediction of Polymers from Weight-Loss Data"
Joseph H. Flynn and Brian Dickens
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"Concentration Dependence of the Diffusion Coefficient of Polystyrene at Theta-Condition"
Charles C. Han
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"Diffusion Coefficients of the 45S and 50S States of the Large Ribosomal Subunit of E. Coli by Quasielastic Light Scattering"
Charles C. Han, I. N. Serdyuk, and Hyuk Yu
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Charles C. Han and Frank L. McCrackin
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"Differential Scanning Calorimetry Studies of Some Analogs for the Lipid Component of Biological Membranes"
J. T. Joseph, Albert Hybl, and Joseph H. Flynn
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"Some Methods of Measurement of an Elastic Strain Energy Function of the Valanis-Landel Type"
E. A. Kearsley
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"Some Non-Linear Effects in Polymer Testing"
E. A. Kearsley
To be published in Proceedings of ASTM Committee D11.36
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"Fabrication of Piezoelectric Polymer Film"
J. M. Kenney and S. C. Roth
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"Aspects and Implications of the Diversity in the Habits Exhibited by Polymer Crystals Grown from Solution"
F. Khoury and L. H. Bolz
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"Substitution in Barium-Fluoride Apatite: The Crystal Structures of $Ba_{10}(PO_4)_6F_2$, $Ba_6La_2Na^2(PO^4)^6F^2$ and $Ba^4Nd^3Na^3(PO^4)^6F^2$"
M. Mathew, I. Mayer, B. Dickens, and L. W. Schroeder
J. Solid State Chem., 28, 79-95 (1979)

"Crystal Structure of a Struvite Analogue, $MgKPO_4 \cdot 6H_2O$"
M. Mathew and L. W. Schroeder
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"Raman Intensities of Longitudinal Acoustic Modes"
J. Mazur and B. Fanconi
J. Chem. Phys. (accepted for publication)

"Monte Carlo Calculations of the Number of Ways to Pack Nonoverlapping Rods on a Square Lattice"
Frank L. McCrackin
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"The Normal Stress Response in Non-Linear Viscoelastic Materials - Some Experimental Findings"
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J. B. McKenna and L. J. Zapas
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"Degradation Resistance of Some Candidate Composite Biomaterials"
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G. B. McKenna and R. W. Penn
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"Dimensional Change of Dental Amalgam and a Suggested Correlation Between Marginal Integrity and Creep"
G. C. Paffenbarger, N. W. Rupp, and P. R. Patel
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Paper presented by Dr. Paffenbarger as introduction to
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Memorial Award of the Ohio Dental Association, Columbus, Ohio,
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G. C. Paffenbarger
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"Acoustic Emission of Polymers under Tensile Load"
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"Surface Tension Theory of Pure Liquids and Polymer Melts"
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J. C. Smith
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J. C. Smith
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"Equilibrium Phase Fields in the Vanadium-Osmium System"
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Seminars for Staff and Guests

Professor C. Macosko
"Rubber Elasticity in Model Silicone Networks"
10/2/78

Professor R. Byron Pipes
"Fracture of Composite Materials"
10/5/78

Dr. J. H. Mason
"A Review of Electrical Discharges in Insulating Materials"
10/20/78

Dr. Philip Geil
"Amorphous Polyethylene"
10/24/78

Professor Guilio Sarti
"A Physical Interpretation for Case II Transport Solvent Induced Stresses and Crazing Kinetics"
11/3/78

Yasuo Suzuoki
"Thermally Stimulated Currents in Polymers"
11/7/78

Professor Kichinoske Yahagi
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[5] DIRECTOR, ADA
[6] PART TIME
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